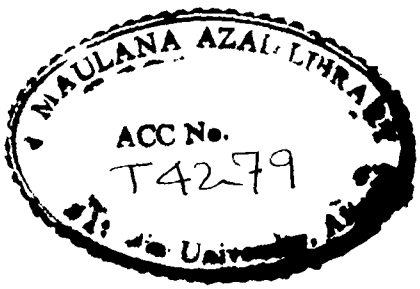

SOME PHYSICOCHEMICAL STUDIES ON ADSORPTION AND ION-EXCHANGE

SUMMARY

THESIS SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

IN

CHEMISTRY

BY

KHWAJA ZUBER ALAM

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202 002 (INDIA)

1991

SUMMARY

The thesis comprises of five chapters. Chapter-I is a General Introduction which takes into account the theory and practice of the adsorption and ion-exchange studies in the context of the present day problem of pollution. A thorough survey of literature of last thirty years on these two aspects is incorporated with a view to highlight the basic problems at hand and their remedy using these methods. The Introduction is followed by a list of 331 references.

The Chapter-II is entitled as "Adsorption of Tertiary Nitrogen Containing Compounds on Activated Carbon: Equilibrium Studies of Nicotinic Acid in Aqueous Systems". In this chapter, adsorption studies of nicotinic acid, a tertiary nitrogen compound, have been discussed on activated carbon at 30, 40, 50 and 60^{o}C in pure water and in the presence of a decimolar NaCl solution. Such types of compounds cause respiratory tract and gastrointestinal disturbances, damage kidneys and liver, and are suspected carcinogens. Various equations for the adsorption isotherms have been tried to fit the adsorption data by using a computer programme, and it has been observed that all the isotherms follow a Langmuirian pattern. The thermodynamic

parameters calculated for both the systems are given in Table-I. The mechanism of adsorption has also been put forward on the basis of these parameters. It has been observed that the adsorption of nicotinic acid on activated carbon in pure aqueous medium increases with the increase in temperature from 40 to 60°C. The total adsorption of nicotinic acid at 30°C shows an abnormal value i.e. between 50 and 60°C which may be due to strong hydrogen bonding between the functional groups of nicotinic acid and activated carbon. A steep rise in adsorption isotherm may be due to surface concentration of nicotinic acid molecules on the surface of AC. It has also been observed that the presence of an electrolyte (NaCl) plays a significant role in the adsorption process.

In Chpater-III the equilibrium studies of 2,6-lutidine on activated carbon in aqueous solutions have been summarized. The studies have been made at different temperatures such as 30, 40, 50 and 60°C in pure water and 0.1 M NaCl solution. The aim of this study is to understand the surface reactions affecting the adsorption of such type of compounds.

Most of the adsorption isotherms observed, show a two step process for each temperature, except at 60°C

in pure aqueous medium. Different equations for different adsorption isotherms have been tried to fit the adsorption data by using a computer simulation technique. The analysis of adsorption data reveals some interesting results. They follow a mixed trend in adsorption pattern. Some obey the Freundlich type behaviour and others the Langmuirian type. The overall thermodynamic paramters have been calculated from the isosteric enthalpy at a particular surface coverage (Table II). On the basis of these parameters a mechanism of adsorption process has been proposed. It has been observed that presence of an electrolyte (NaCl) increases the total adsorption of 2,6-lutidine on activated carbon.

Chapter - IV is entitled as "Equilibrium Studies for the Forward and Backward Metal-H(I) Exchanges on Antimony(V) Arsenophosphate". As we know the ion exchange equilibria are of great practical and theoretical importance and have the subject matter for a large number of studies ever since the ion exchangers were recognized as such. The appropriate means of describing equilibria is on the basis of thermodynamics. Hence the thermodynamics of ion-exchange on synthetic inorganic ion exchangers has been of great interest among the scientists in the recent years.

This chapter contains the results of equilibrium studies on amorphous antimony(V) arsenophosphate for the forward and backward exchanges of Fe(III), Cu(II), Ni(II), Hg(II) and Mn(II), which are some of the important pollutants, at 30 and 50°C. The selectivity of the H(I)/Metal and Metal/H(I) exchanges has been studied at a constant ionic strength of 0.03 on antimony(V) arsenophosphate. On the basis of ion-exchange isotherms, various thermodynamic parameters have been calculated (Tables III, IV), and some predictions are made for the exchange processes taking place in the material. The overall order of uptake of different metal ions is:

$$Fe(III) > Ni(II) > Mn(II) > Cu(II) > Hg(II).$$

The above sequence suggests that the exchange of these metal ions occurs in the unhydrated form. They shed away most of their water of hydration at the surface of exchanger and get hydrated again after being exchanged.

In Chpater-V the evaluation studies of the dimensionless time parameter for some particle diffusion controlled forward and reverse H(I) - Cation(I), OH(I)-anion(I) and OH(I) - anion(II) exchanges have been made. In addition to the ion-exchange procedures in which a high

selectivity for a particular ions are required, new applications in the area of heterogeneous catalysis, solid electrolytes, inorganic ion-exchange membranes, ion-selective electrodes and intercalation compounds can be explored. In most of these fields, information of ion-exchange kinetics and mobility of counter ions in the lattice structure are needed. The kinetic parameters are important to understand the mechanism on the surface during the ion exchange process for which a knowledge of the dimensionless time parameter, τ , for the various mobility ratio is essential and makes the calculations much easier.

In the past,the practice had been to determine the τ values by the graphical method, which was not accurate. Also, it is not applicable to a true ion exchange process. The present study illustrates a novel procedure for such an evaluation which is based on the explicit expressions given by Helfferich and represents a true ion exchange process. The tables illustrate the τ values calculated by a computer simulation technique for both the forward and reverse ion-exchange processes for the monovalent cations and anions and bivalent anions against the H(I) and OH(I) ions respectively.

TABLE I

Thermodynamic parameters at different temperatures for the adsorption of nicotinic acid

T (°C)	Pure aqueous medium[a]			0.1 M NaCl medium[b]		
	ln K	ΔG (kJ mol^{-1})	ΔS (kJ $mol^{-1}K^{-1}$)	ln K	ΔG (kJ mol^{-1})	ΔS (kJ $mol^{-1}K^{-1}$)
30	-0.3403	0.8572	-0.0250	-0.1616	0.4071	0.1325
40	0.9580	-2.4931	-0.0135	-0.6121	1.5927	0.1283
50	-0.0051	0.0137	-0.0208	0.8128	-2.1828	0.1360
60	-0.3210	0.8889	-0.0228	1.0381	-2.8741	0.1340

[a] ΔH = -6.7257 kJ mol^{-1}.

[b] ΔH = 41.7477 kJ mol^{-1}.

TABLE II

Thermodynamic parameters for the adsorption of 2,6-lutidine on activated carbon at a surface coverage of 2.6 mmol g^{-1}

T (°C)	Pure aqueous medium[a]			0.1 M NaCl medium[b]		
	ln C_e	ΔG_m (kJ mol^{-1})	ΔS_m (kJ $mol^{-1}K^{-1}$)	ln C_e	ΔG_m (kJ mol^{-1})	ΔS_m (kJ $mol^{-1}K^{-1}$)
30	2.8950	-7.2929	-0.0801	2.7200	-6.8510	-0.0834
40	2.5600	-6.6618	-0.0795	2.2650	-5.8942	-0.0838
50	2.1400	-5.7468	-0.0799	1.9050	-5.1157	-0.0836
60	1.7800	-4.9280	-0.0800	1.5600	-4.3190	-0.0835

[a] ΔH_m^{ads} = -31.0380 kJ mol^{-1}

[b] ΔH_m^{ads} = -32.7010 kJ mol^{-1}

TABLE III

Thermodynamic values of Ni(II)-H(I), Mn(II)-H(I), Hg(II)-H(I), Fe(III)-H(I) and Cu(II)-H(I) exchanges at 30 and 50°C on antimony(V) arsenophosphate cation exchanger

Thermodynamic parameter	Values for the Ni(II)-H(I) system at		Values for the Mn(II)-H(I) system at		Values for the Hg(II)-H(I) system at		Values for the Fe(III)-H(I) system at		Values for the Cu(II)-H(I) system at	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
K	37.62	52.47	22.98	27.23	15.56	16.38	23.38	32.87	25.06	27.58
ΔG^{o} (KJ mol^{-1})	- 9.14	-10.65	-7.89	-8.87	-6.93	-7.51	-7.94	-9.38	-8.12	-8.91
ΔH^{o} (KJ mol^{-1})	5.86		6.88		2.08		13.82		3.88	
ΔS^{o} (K $mol^{-1}K^{-1}$)	49.51	51.14	48.74	48.76	29.70	29.69	71.81	71.83	39.60	39.59

TABLE IV

Thermodynamic values of H(I)-Ni(II), H(I)-Mn(II), H(I)-Hg(II), H(I)-Fe(III) and H(I)-Cu(II) exchanges at 30 and 50°C on antimony(V) arsenophosphate cation exchanger

Thermodynamic parameter	Values for the H(I)-Ni(II) system at		Values for the H(I)-Mn(II) system at		Values for the H(I)-Hg(II) system at		Values for the H(I)-Fe(III) system at		Values for the H(I)-Cu(II) system at	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
K	0.99	1.68	0.26	0.36	0.25	0.26	0.46	0.61	0.23	0.24
ΔG^{o} (KJ mol^{-1})	0.25	-1.39	3.39	2.74	3.49	3.62	1.93	1.34	3.70	3.60
ΔH^{o} (KJ mol^{-1})	9.32		13.19		1.59		11.45		1.73	
ΔS^{o} (J $mol^{-1}K^{-1}$)	29.90	33.00	32.36	32.37	6.30	6.20	31.40	31.20	6.52	5.85

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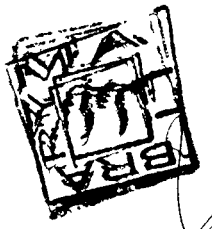

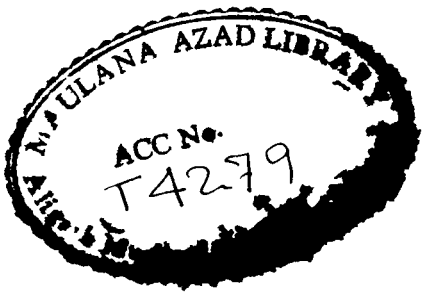

TO

MY PARENTS

K. GOPAL VARSHNEY
M. Sc., Ph. D.
READER
DEPARTMENT OF APPLIED CHEMISTRY

Phone : (Off.) 0571-6042
FACULTY OF ENGG. & TECHNOLOGY
ALIGARH MUSLIM UNIVERSITY
ALIGARH-202 002 (INDIA)

Dated: 17.6.1991

CERTIFICATE

This is to certify that the work embodied in this thesis is the original contribution of the candidate and is suitable for submission for the award of Ph.D. degree in Chemistry of Aligarh Muslim University, Aligarh.

(K.G. Varshney)
Supervisor

ACKNOWLEDGEMENT

At the very outset, I pay homage to late Professor Mohsin Qureshi who was the sole inspiration to me and who guided me for this endeavour.

I place on record my deep sense of gratitude to Dr. K.G. Varshney, Reader, Deparment of Applied Chemistry, for his constant encouragement, unflinching support and excellent supervision which enabled me to finalize all my investigations. I sincerely thank Prof. M. Ajmal, Chairman, Department of Applied Chemistry, who not only provided me with necessary research facilities rather took a keen interest in my work.

I am equally grateful to my erudite teacher, Dr. Anees Ahmad, Lecturer, Department of Chemistry, whose constant support and counsel enabled me to give this task its present shape.

I must express thank to my friends and colleagues Dr. A.R. Khan, Dr. A.H. Khan, S.B. Singh, M.S. Siddiqui, Dilshad, Tabassum and Sehba for their cooperation, benevolence and advice.

I am indebted to my uncle Mr. A.M. Shamsi for his keen interest in my academic pursuits and his valuable

guidance. I am equally thankful to all of my family members for their great affection and care.

I thank Mr. H.S. Sharma who typed the manuscript meticulously with infinite patience.

Finally, I thank University Grant Commission (India) for the award of a fellowship.

(KHWAJA ZUBER ALAM)

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CHAPTER - I

GENERAL INTRODUCTION

Environmental problems and their control have received a great deal of interest and publicity now-a-days. The scientists have come to realize that this is very complex area. While many advances have been made in recent years, much is yet to be learned concerning pollution. Analytical Chemistry plays a very important role in both dealing and controlling environmental pollution. It can be thought as comprising of two branches, qualitative and quantitative. Qualitative analysis deals with finding what constituent or constituents are in analytical sample, and quantitative analysis deals with the determination of how much of a given substance is in the sample. With today's instrumentation and with a large variety of chemical measurements available, specificity or sufficient selectivity can often be achieved so that the quantitative measurement serves as a qualitative measurement.

Adsorption and ion-exchange are the two important conceptions in analytical chemistry since the solid-liquid interactions have always been of interest because of their diversity and immense applications. Interactions between the components of liquids or solutions and surfaces of the solids make, in a wide variety of ways, a momentous contribution to our everday life. Its importance in the petroleum, chemical and pharmaceutical industries is well established. However, recent activities in biotechnology,

medicine, biomedical, biochemical, environmental and polymer engineering have broadened the usefulness of processes. Similarly, ion-exchange is one of the most versatile analytical technique in separation science. Various applications of ion-exchange procedures are in the field of heterogenous catalysis, radio chemical analysis, solid electrolytes, inorganic ion-exchange membranes, environmental studies, ion-selective electrodes and intercalation compounds.. In the following sections an attempt has been made to report the developments made so far in the theory and practice on these two aspects of study.

A. ADSORPTION

Adsorption is a fundamental natural process. Since the molecules on the surface have an environment different from those in the bulk of material, the surface has a different free energy from the bulk of the material (1). When the molecules of a gas or liquid are concentrated on the surface of a solid the molecules are said to be adsorbed on the solid surface. This is a surface phenomenon and is different from "Absorption" which is the penetration of one component through the body of another. The material that is adsorbed on to the surface is called the 'adsorbate' and the underlying material as 'adsorbent' or 'substrate'.

Adsorption is sometimes classified as physical and chemical. The physical adsorption is called as "physisorption" and chemical adsorption as "chemisorption". In the former the molecules are adsorbed on a solid surface by essentially the physical forces. In chemisorption, however, the molecules form the chemical bond with the solid surface. In case of the physical adsorption the van der Waal's interactions (for instance, dispersion or polar interactions) play an important role between the adsorbent and adsorbate molecules. They are the long but weak interactions. The amount of the energy, when a molecule is physisorbed, is of the order of enthalpy of condensation. This energy can be absorbed as vibrations of the lattice and dissipated as heat. A molecule bouncing across the surface will lose its kinetic energy and stick to the surface resulting in the rise of temperature of the system i.e. heat is evolved.

In chemisorption, the molecules stick to the surface as a result of the formation of a chemical and usually a covalent bond and tend to find the sites resulting in an increase of the coordination number with the adsorbent. The energy of attachment is very much greater than in physisorption. In chemisorption the surface enters into reactions as a catalyst. This type of catalysis, called heterogenous

catalysis, is understandable only on the basis of some of the informations deduced in adsorption studies. Similar conclusions, that are drawn from the chemical reactions on a surface, help to answer some of the problems unsolved by adsorption studies. The photoelectron spectroscopy (ESCA) can be applied to reveal some of the bonding properties of the adsorbed species. In surface studies this is normally referred as photoemission spectroscopy. Varities of vibration spectroscopy also reveal the nature of the adsorbed species, and in particular whether the dissociation has occurred. Infrared absorption spectra can be obtained by using infrared transparent materials and a technique that involves the internal reflection.

Adsorption is essentially a phenomenon of separating surface and the interfacial tension (2). It is generally governed by the thermodynamic relation:

$$\triangle G = \triangle H - T \triangle S \qquad \ldots\ldots\ldots (1)$$

$\triangle G$, $\triangle H$ and $\triangle S$ are taken, respectively, as the free energy, heat and entropy changes in the process. Since adsorption leads to a decrease in the free energy, $\triangle G$ is negative. The adsorbed molecules move from a three dimensional region to a two-dimensional one, which causes a decrease in

entropy, i.e. $\triangle S$ negative. Thus, $\triangle H$ must also be negative, which is usually the case. So, adsorption is generally exothermic. However, the conditions in solute adsorption are more complicated. Giles et al. (3,4) have reported endothermic adsorption in case of a solute forming large ionic-micelle (e.g. dyes). Josef et al. (5) also found an increase in the isosteric heat of adsorption with an increasing surface coverage in the adsorption of aliphatic amines on alumina. The athermic adsorption covers those cases which do not give measurable heat of adsorption. It is generally the case in ion exchange adsorption of solutes, which do not form large micelles. By definition, the ion-exchange sorption of ions is accompanied by the release of equivalent quantity of ions by the sorbent to the external solution. This distinguishes ion-exchange process from the major sorptive mechanism i.e. physisorption and chemisorption.

The reverse process (i.e. desorption) measures the resistance of the systems to change, and manifests itself as a binding force between the adsorbate and adsorbent. The binding forces involved may be of several types, such as van der Waal's, ion exchange, covalent bond formation and hydrogen bonding, depending on the nature of the substrate surface and the adsorbate.

In the context of adsorption of polar compounds, it can be said that the binding forces are sorbate-substrate bonds. Adsorption of the organic ions may then be controlled by van der Waal's forces, electrical interactions like coulombic, dipole or hydrophobic interactions, operating on the uncharged groups of the ions (i.e. reversible) as well as by the electrical forces, operating on the charged groups (chemical interaction, irreversible). When both the adsorbate (e.g. amino acids) and the adsorbent (e.g. hydrous oxides) bear a charge, attractive forces can operate, and possibility of ion-exchange cannot be ruled out (6).

The surface structure of a solid is controlled to a large extent, by the underlying bulk structure which, in turn, is defined by chemical composition and crystal structure. The various surface groups on the common polar adsorbents may ionize in the presence of water or similar solvents leaving a net charge or so called zeta-potential on the surface of the adsorbent. This surface charge has been claimed by many workers (7,8) to have an important effect on the sorptive properties of an adsorbent, especially where ion-exchange plays an important role.

Adsorption Isotherms:

Most of the studies on adsorption from solution have been concerned with equilibrium conditions, and predominantly with the adsorption isotherms. An adsorption isotherm describes the equilibrium relationship between the adsorbed and unadsorbed sample, at a given temperature. It is a plot of the concentration of "X" in the adsorbed-phase versus concentration of "X" in the unadsorbed phase. The interest in these isotherms lies in the amount of information they can yield, viz., identification of the adsorption mechanism, heat of adsorption, specific surface area of the porous solid, diagnosis of the orientation of the solute molecules at the surface, and its degree of self-association.

The earlier attempts (9) of classification of isotherms have served for quite a long time. Four types of isotherms are identified on the basis of the shape of the initial part of the isotherm. This classification of isotherms had been reported and theoretically explained by Giles et al.(7,10) on the basis of solid-solution interface. Various shapes of the isotherms considered are shown in Figure 1.1. and can be characterized as follows:

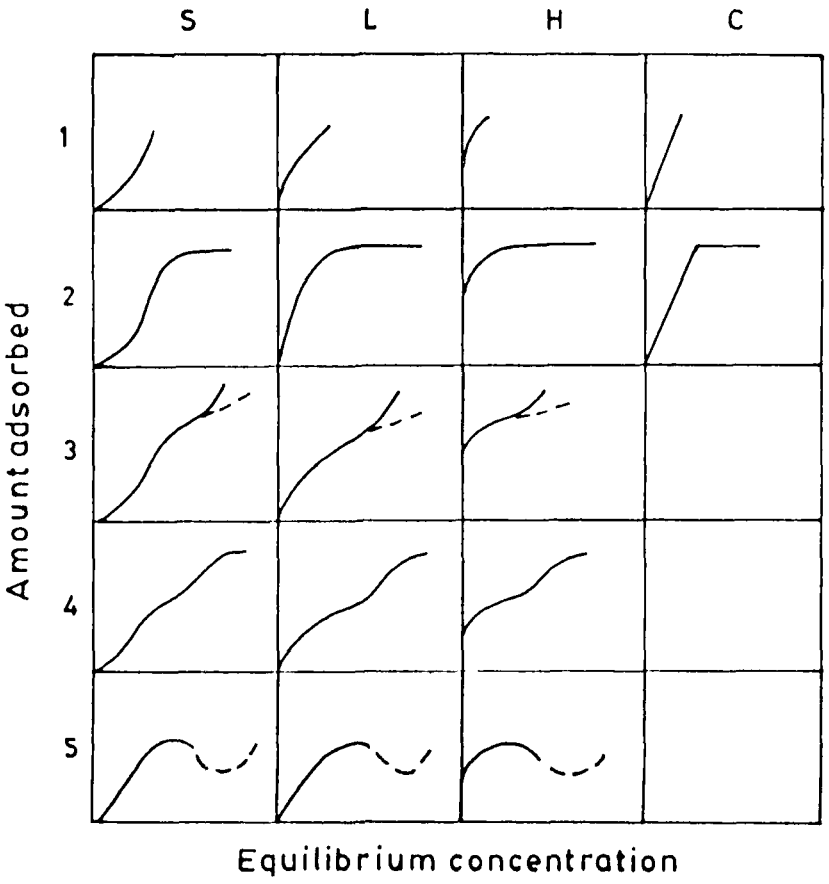

Fig. 1.1: CLASSIFICATION OF ISOTHERM SHAPES

i) Langmuir or L-type isotherms,

ii) S-type isotherms,

iii) High affinity or H-type isotherms, and

iv) Constant partition or C-type isotherms.

The L-type isotherms are most common. They are characterized by an initial region which is concave to the concentration axis. They are obtained when there is no strong competition from the solvent for sites on the surface. The curves refer to those cases in which the most active sites are initially covered, but the ease with which adsorption takes place decreases until a monolayer is completed.

For the S-type isotherms the initial region is convex to the concentration axis which is frequently followed by a point of inflection leading to an S-shaped curve. These isotherms indicate that:

i) The solvent is strongly adsorbed,

ii) There is strong intermolecular attraction within the adsorbed layer, and

iii) The adsorbate is monofunctional.

The second condition is most likely obtained if the major axis of the adsorbed molecules is perpendicular to the surface. By a monofunctional adsorbate we mean here that

the molecule has a single point of strong attachment in an aromatic system or an aliphatic system of more than five carbon atoms. Further, the adsorbate is not micellar. In many cases, the S-curve indicates a 'cooperative adsorption' with solute molecules tending to be adsorbed, packed in rows or clusters.

The H-curve occurs when there is a high affinity between the adsorbate and adsorbent, which is shown even in very dilute solutions. Thus, it can result from the chemisorption or from the adsorption of polymers or ionic micelles, though other special cases are known.

Finally the C-type isotherm has an initial linear portion which indicates a constant partition of the solute between the solution and the adsorbent and occurs with the microporous adsorbents.

The isotherms have a great utility in diagnosing the mechanism of adsorption, and also in distinguishing the probable configuration of the adsorbed molecules (7). Thus, S-curve indicates a vertical orientation, L-curve shows the flat orientation and strong intermolecular interaction, while H-type isotherm is assumed to be typical of sample micelle formation. However, such a generalisation

needs great care, as many other factors also contribute to the isotherm's shape (11).

The adsorbents which have been commonly studied earlier are fly ash (12-17), peat (18-23), fibrous keratinous materials such as wool and hair (24-26), clays (27,28), alumina bauxite (29), woolastonite (30,31), discarded automobile tires (32), suspended particles of river water (33-35) and sludge (36-42). Some other adsorbents have been proved quite useful viz. alumina, silica, carbon and cellulose (43). In addition to these, some adsorption studies have also been reported on tin oxide, titanium oxide, thorium oxide and zirconium oxide (44).

Out of them carbon is probably the most interesting one. It occurs in a variety of forms e.g. graphite charcoal, graphitised carbon black and bone charcoal etc. Activated carbon (AC), usually in the form of charcoal, is sometimes used for a chromatographic column. It has a great affinity for all types of solutes because its surface contains not only carbon in its graphite lattice, but also a variety of polar and ionic groups. It contains a carboxylic group and exchangeable hydrogen ions. So AC plays a role of a weak cation exchanger also. The simple adsorption behaviour of carbon was explored by Garten and Weiss (45) while the

adsorptioion exchange properties of pure graphite were investigated by Galbraith (46). The AC filled with inorganic materials has also been used as an adsorbent in addition to the simple AC.

Some Recent Studies on the Adsorption Properties of Activated Carbon:

The numerous studies on the adsorption of different types of organic and inorganic substances on activated carbon are summarized below:

Adsorption of hydrocarbons:

Koval'skaya et al. (47) have studied the adsorption of aromatic hydrocarbons on activated carbon (AC) and measured the adsorption capacity on the dry and damp sorbents. They showed that the capacity decreases with an increase in the moisture content. The adsorption capacity for paraffins and cycloparaffins on the steam-activated carbon at high temperature was studied using a micro-chromatographic method by Selim et al. (48). Pirbazari et al. (49) have studied the selective removal of benzene from water with the help of the activated carbon in presence of other organic substances such as humic acid, while Kim et al. (50) have studied the removal of toluene from air using

powdered activated carbon/water slurry reactor. A mini dynamic adsorption technique was developed by Bilello et al. (51) for determining carbon adsorption capacities. Kitagawa measured the breakthrough curves for hexane and benzene solutions and ethane (52,53). He found a linear relationship between the breakthrough time and bed volume (52). In case of ethane, surface diffusion is the predominant intraparticle transport process at lower temperatures (53). Andreev found a correlation between the adsorption coefficients of potassium salts of nitroalkanes and their degrees of hydration and polarizabilities. Adsorption increases in order of $KCH_2NO_3 < KCH(NO_3)_2 < KC(NO_2)_3$ which parallels the order of decreasing free energy of hydration (54).

The thermodynamic behaviour of various hydrocarbons and some other organic compounds for the adsorption on AC and graf pack graphitised carbon (GGC) has been studied by Ikuo et al. (55) and Sukhorukov (56) respectively. Ikuo proposed the mechanism of adsorption in terms of free energy changes according to which the adsorption occurs via precipitation inside the pores of adsorbent. On the other hand Sukhorukov calculated the heat of adsorption and Henry's constant from gas chromatographic retention data. He reported high selectivity of GGC for the alkane

and aromatic hydrocarbons. Jaroniec et al. measured the equilibrium adsorption isotherms of ethane and benzene on two different types of ACs by the dynamic and static methods and discussed the energetics of heterogeneity of adsorbents (57). Gas-solid chromatographic technique was used by Garcia et al. to study the high temperature adsorption of hydrocarbons on AC obtained from agricultural byproducts (58).

Micro calorimetric technique was used to characterize two types of ACs through aromatic hydrocarbon adsorption isotherms and densitometric measurement by Kreiver et al. (59). Du et al. conducted NMR study to examine the mechanism of adsorption of hydrocarbons on several types of ACs (60,61). They reported a capillary condensation mechanism of adsorption in the micropore with a diameter $<30\ ^{o}A$ and mono/multilayer adsorption on the solid surface of pores with a diameter $>30\ ^{o}A$. They further explained that the exchange of protons on the surface acidic groups with the adsorbed species, makes an important contribution to the relaxation process.

Madey (62) examined the time dependence transmission of hydrocarbons at low concentrations through activated carbon and polystyrene adsorbed bed both theoretically and

experimentally. He formulated the theory of adsorption of radioactive gases and its mixture with hydrocarbons on heterogenous microporous solid. The adsorption from solutions was also examined. On the other hand, Leggetler et al. (63) used the molecular dynamics simulation technique to compute the various functions of the adsorbed hydrocarbon molecules on a structured graphitic surface. They reported in and out of plane velocity, auto correlation function, surface diffusion coefficient, angular velocity, reorientation correlation function and time correlation function associated with the conformation at dynamics of their flexible molecules.

Adsorption of alcohols:

The use of AC for the adsorption of aliphatic and aromatic alcohols has been studied by many researchers. Rozwadowski determined the sorption and desorption mechanisms with the help of thermodynamic and kinetic measurements (64,65). Adsorption isotherms of alcohols have been reported on activated, granular and fibrous carbons (66-68). A modified Langmuir equation is given to describe the adsorption of dissolved solids by AC where the theory and the experimental results show a good agreement (69). Gorchakova

et al. (68) proposed the effect of temperature on the molecular rearrangement of adsorbed alcohols on BAU carbon. The breakthrough curve and its dependence on bed length has also been reported. Osipov et al. (70) demonstrated the use of different ACs for the removal of alcohols from industrial wastewater. Zabasajia et al. (71) reported the electrosorption of n-alcohols on graphite particles and developed an experimental method to estimate the isotherm parameters. They demonstrated with the help of theoretical treatment, that the extent of adsorption increases with the increase in double layer capacitance of interface and size of organic species.

Adsorption of Phenols:

Adsorption of phenols from dilute aqueous solutions on porous and nonporous carbon and activated carbon have been reported in literature. Mahajan et al. (72) studied the effect of temperature on the nature of carbon surface and the adsorption of phenols. Yasushi et al. (73) studied the effect of concentration on the adsorption behaviour of phenols and found a typical breakthrough curve. The thermoanalytical studies on AC for adsorption and desorption of phenols was conducted by Vincenzo et al. (74). Grant examined

the effect of physicochemical properties of adsorbents on the irreversible adsorption behaviour of these phenolic compounds (75,76). The effect of microporosity of adsorbents was studied for substituted phenols by Caturla et al. (77). Massaki measured the adsorption rates of p-nitrophenol, benzophenol and p-chlorophenol from dilute solution (78) whereas Sheindrof did the same for p-bromophenol and other phenols during wastewater treatment by AC, where Freundlich adsorption isotherms are applicable (79). Use of ACs and their efficiency in the removal of phenols from wastewater was also reported by Lu et al. (80) and Paprowiez (81). Russel et al. (82) conducted the equilibrium studies for different phenols and found a fast attainment of equilibrium with powdered AC as compared to the granular one. Le Cloirec et al. (83) conducted the solid state ^{1}H NMR studies on phenol saturated and unsaturated samples of four ACs to know the quantification in exchange behaviour of portions of the adsorbents. They also reported the maximum adsorption capacity of AC as 100 mg/g for phenol.

Adsorption of organic acids:

Chubarova et al. (84) studied the sorption capacity of AC for adipic acid from aqueous solution under cyclic operation conditions. Jain et al. (85) reported the adsorption of fumaric and maleic acids on sugar charcoal to be a discontinuous process. The fate of fulvic acid

during the water treatment was studied by Breeman et al. (86), while its identification by adsorption on AC was studied by Stanislaw et al. (87). The relative rates of adsorption of acrylic and protonic acids were studied by Khan et al. (88).The adsorption equilibria of some organic acids and bases from aqueous solution on AC was studied by Onal et al. (89). They tested the validity of traube rule for the process which states that the adsorption of organic substances increases regularly through a homologous series.

Adsorption of Dyes:

Now-a-days dyes are also being removed from dying effluents by adsorption on AC from coal. The temperature, the nature of the dye and AC and the presence of some electrolyte have marked effect on their adsorption behaviour. Increase in temperature and the addition of NaCl increases the adsorption rate and lengthens the breakthrough time of the dyes (90). Kuwabara reported the adsorption superiority of carbon mineral adsorbents over common AC in the removal of direct blue, congo red and indigo ceramine dyes from wastewater (91). Similarly, Mamchenko et al. (92) have reported the adsorption behaviour of associated dye stuffs

towards nonuniform porous carbon adsorbents. Gorden proposed a three step adsorption model for the adsorption of dyes on AC (93-95). The various kinetic studies were also conducted on the adsorption of different dyes namely, victoria blue, disperse blue-7 etc. (96,97).

Adsorption of Pesticides and Pollutants:

Various adsorption studies of pollutants and pesticides have earlier been carried out on AC. Yoshitaka et al. (98) studied the effective surface diffusitivites of aqueous solutions of chlorinated organics in water on AC using different concentrations. Il'Yasov et al. (99) proposed the mechanism of adsorptions using an isothermic model of adsorption. Radeka et al. (100) reported the comparative adsorption behaviour of dichloromethane from gaseous and aqueous phases. They have observed that the adsorption capacity from aqueous solution was smaller than from the gaseous phase due to the competitive water adsorption. The fate of adsorption of chloropicrin and the displacement of preadsorbed water from BPL carbon was given by Hall et al. (101). The adsorption of p-nitroaniline from aqueous solutions by a thick layer of active carbon of varying porous structure and its mechanism was reported by Mamchenko et al. (102).

Lagana et al. (103) studied the behaviour of fifty one compounds on graphitised carbon. They determined the sorption capacities and the extent of recoveries for the chlorinated pesticides. The irreversible adsorption of lower aliphatic amines on pure AC surface was studied by Roman et al. (104). The effect of pH on adsorption of dissolved organic acids, bases, anionic and cationic surface active agents, nonionic organic compounds and polymers from industrial effluents were studied by Wang and Martin (105,106). The pH effect becomes more significant as the acidity and basicity of the adsorbate in solution increases (106).

The adsorption of alfatoxin B_1, the lung and gastro-intestinal toxicant was studied by Walter et al. (107) and effective conditions were determined. Kaplin observed (108) that AC is capable of adsorbing staphtococial toxin at a rate of 7.7 unit toxin/g of carbon. The adsorbing capacity of AC increased $\geqslant 3$ fold when the carbon is coated with antistaphtococial γ-globutin fraction or human hyper immune plasma. Luzhnikov studied (109) the bare plasma coated AC for the adsorption studies of barbital and barbiturates and made a comparison of the two adsorbents. Mckay et al. studied the adsorption of PhOH, p-chlorophenol, sodium dodecyl sulfate and Hg from wastewater on AC (110,111).

Whitaker et al. (112) has used the isothermal and continuous flow column systems for the adsorption studies of selected pesticides by AC. While Farran et al. (113) conducted the similar studies on F-400 AC using a flow injection HPLC system. . Lovett and Peltorak (114) reviewed the use of AC for the control of odourous air pollutants. The AC impregnated with quinilidine has been used for removing the alkylhalides contaminants from gas stream by Julius et al. (115). The use of AC for the treatment of municipal, industrial, and waste waters have been reviewed in detail with a large number of references in literature (116-118). Janina et al. have removed the benzo(a) pyrene from water by using granular AC. They have observed the Freundlich adsorption isotherm under static conditions (119). Numerous predictive models (102, 120-126) have been developed to explain the surface and bulk adsorption of organics and inorganics on AC. The behaviour of adsorbates and adsorbents, the sites of adsorption, single and multicomponent adsorption and desorption systems were studied and their mechanisms proposed and tested accordingly (127-138).

Many research papers, purely theoretical in nature, have appeared describing the kinetics and thermodynamic

behaviour of different adsorbates on AC (139-147). Seigfried (143) has reviewed in a synopsis of 35 pages, the method of calculation of breakthrough curves for the adsorption kinetics of organic pollutants in air on AC. The Polanyi potential adsorption theory and its application to adsorption from water solution on AC has been reviewed by Milton Manes (148-149). A significant use of this theory and that of the solvophobic theory have recently been reported by Altshuler et al. and Arbuckle (150,151).

Adsorption of inorganics on AC:

Different types of studies have been conducted to determine the adsorbability of inorganics on AC surface. The potentiometric studies on AC and carbon black immersed in aqueous solution of electrolytes were conducted by Helena et al. (152). The samples studied were subjected to various modified treatments : demineralization, oxidation in liquid and gaseous phases, saturation with hydrogen and degassing etc. The contact time, the amount of anions in the solution and change in pH have a marked effect on the potential of carbon. The adsorption of strontium on AC indicates that it increases with equilibrium time and at pH 1.5-3 (153). Gerard (154) made the magnetic susceptibility measurements on the sorbate-sorbent system to detect

sorption mechanism. Vilinskaya (155) proposed a qualitative model of electrolyte adsorption in porous materials. Attempts have also been made to predict the microporosity and adsorption characteristics of AC, which are reviewed by Katsumi and Dubinin (156,157). Tsunoda measured the pore width of various ACs by adsorption of water vapours (158).

Kraus et al. (159) performed the adsorption experiments of acids from concentrated electrolytes by AC. The studies included the removal of HNO_3 from $LiNO_3$ solutions, HCl from NaCl and LiCl solutions, and $HClO_4$ from $NaClO_4$ solutions. The H_2O in the carbon pores was related to a H_2O-organic solution model. Huang (160) removed Cr^{6+} from electroplating and metal finishing wastewaters effectively with the help of AC. He also reviewed the chemical interactions between inorganics and AC (161). A comparative study of adsorption of Cd(II) and Pb(II) from wastewater by a common AC and AC derived from coconut shell, was conducted by Asulanantham et al. (162). They reported the superiority of the later in the wastewater treatment. Ryszard and Witold (163) used AC as anode for electrode position of Ni, Cu, and Zn.

The sorption of Cl^-, Br^- and I^- from aqueous methanol solutions on AC pretreated with HF and NaCl was

reported by Jankowska et al. (164). Yankovska et al. (165) explained the adsorption of these ions through the ion-exchange mechanism with the formation of charge transfer surface complexes with acceptor characteristics of the carbon surface. The adsorption isotherms of I_2 solution in different pure organic and organic solvent mixtures were reported by Swiatkowski and coworkers (166). The characteristics and mechanism of iodine sorption from aqueous, H_2O-organic and organic media were studied and discussed in terms of charage transfer complex with carbon as well as with the solvents (167).

The AC has also been utilized in the purification of air from inorganic gases and vapours. The vapours of ammonia and acids were removed as air impurities by Krokov (168). The adsorption and desorption isotherms of H_2S in micropores of AC show a hysteresis phenomenon(169). The adsorption isotherms of NO_2, CS_2 and H_2S were determined by Hoppe et al. (170) on AC. The surface characteristics and their role in adsorption and desorption of SO_2 was examined by Davini (171). Andriew et al. (172) determined the rate parameters for adsorption of CO_2 in beds of carbon particles by the pulse response method. Shibata et al. (173) reviewed the applications of AC to radiochemical analysis

and adsorption behaviour of various elements in acidic and aqueous media.

Activated carbon filled with inorganic materials:

Inorganic materials have long been utilized in the removal of impurities from water and waste waters, where the surface and/or bulk adsorption takes place. The ion-exchange mechanism has been found to play a significant role in these processes.

Kraus et al. in 1974 reported (174) that AC can be used as a carrier for inorganic adsorbents which by themselves are difficult to prepare in the forms suitable for column operations. The 'filled AC' combines the hydraulic properties of the granular AC with the specific adsorptive properties of the 'filler'.

Activated carbons as carriers for finely divided inorganic adsorbents seem attractive. They are low cost materials and widely available in a variety of mesh sizes. They are highly porous and can hold large amounts of filler. Kraus et al. made a greater contribution in this direction and prepared for the first time iron oxide (hydrous Fe_2O_3 and Fe_3O_4) filled AC. With Fe_3O_4 the object was to prepare an activated carbon which would

exhibit magnetic properties without impairment of 'conventional' adsorption. With Fe_2O_3 they showed that adsorptive capacity for strontium was greatly increased reflecting the property of the use of hydrous oxide. They also prepared (175) the ACs filled with ZnS and CdS and reported that ZnS-AC was an excellent adsorbent for Ag. It was proposed that three different types of diffusion reactions control such an adsorption. Kraus et al. (176) extended their studies with the preparation of SnO_2 filled AC. This material was found to have an unusually high selectivity for lithium permitting its separation from the other alkali metals. They have also prepared (177) AgCl-filled AC, which was selective for I^-.

Ohashi et al. prepared Mo(VI) and Fe(III)-filled ACs and conducted the studies (178) for the adsorption of orthophosphates on these materials.

B. ION-EXCHANGE

Ion-exchange basically involves the combination of mass action equilibria. Ion exchanger is an insoluble material which consists of a charge matrix and exchangeable ions. The exchangeable ions which have the charge opposite to the matrix are called "counter ions" and those which have the same charge as the matrix are called "coions".

If an ion exchanger, containing exchangeable 'A' ions, is brought in contact with a solution containing 'B' ions then the exchange process may be represented by the equation:

$$\bar{A} + B \rightleftharpoons \bar{B} + A$$

Where barred symbols denote the ion exchanger phase. Since it is a reversible process an equilibrium is conventionally set in which some of the ions initially present in the exchanger phase have been replaced by the ions from the solution phase. Ion exchangers are, thus, the insoluble materials carrying the exchangeable cations or anions that can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign which come in contact with an electrolyte solution. The ion exchangers are classified on the basis of the charge of the counter ions. Carriers of exchangeable cations are called as "cation exchangers" and those of exchangeable anions "anion exchangers". The materials capable of both cation and anion exchange are called as "amphoteric ion exchangers".

Ion-exchange is one of the most versatile of all separation methods. It can be applied to microanalysis as well as to macroanalysis. Perhaps its most spectacular

achievement was the separation of rare earths in hitherto unknown impurity (179-185). Ion-exchange chromatography has played an important role in the isolation and identification of the new transuranium elements (186-191) and has even been used for enrichment of isotopes (192-197). Organic substances such as amino acids (198-206), peptides (201,207,208), proteins (201,209), nucleic acids (210), alcohols (201,211,213), glycols (211,213,214), carbonyl compounds (201,211,215,216), carbohydrates and derivatives (201,217-221), ethers (216, 222), amines (201,222-224), hydrocarbons (216,225) and phenols (216,226) have been separated in ion-exchange columns. All these separations were achieved on organic resins. The selectivity was obtained by varying pH and/or by the use of complexing agents. As far as the practical applications are concerned, organic resins are so far the most important ion exchangers. The more recent analytical applications of ion-exchange resins include the collection of selenium(IV) (227), ppb level of aluminium (228) preconcentration of cobalt (229), trace determination of trimethylselenonium in urine (230), molybdenum (231) and iron (232), preparative fractionation of petroleum heavy ends (233), determination of Pt and Pd (234), analysis of metamict minerals containing U, Ti, Nb and rare earths (235) and

the determination of low level of Br^- in fresh water (236). Ion-exchange has also been used with success in food industries (237) and for determining the polar organic in shell process waters (238). The main disadvantage of organic ion exchangers is that they are unstable at high temperatures and in the presence of ionizing radiations. They show signs of degradation with increase in temperature. Changes in their capacity and selectivity occur on exposure to radiations. The inorganic ion exchangers do not suffer from these limitations.

Hence there has been an increasing activity in the field of synthetic inorganic ion exchangers during the last forty years. These materials can be used for high temperature separations of ionic components in radio active wastes. Inorganic ion exchangers also find applications in the analysis of alloys (239,240) and rocks (240,241), separation of metals from drugs (242,243), and in the detection of iron and molybdenum (244,245).

According to their chemical nature and structure synthetic inorganic ion exchangers may be classified mainly into six groups:

i) Insoluble acid salts of polyvalent metals.

ii) Hydrous oxides of polyvalent metals.

iii) Salts of heteropolyacids

iv) Insoluble metal ferrocyanides

v) Synthetic aluminosilicates.

vi) Miscellaneous inorganic ion exchangers, e.g. mercarbide salts and potassium polyphosphates.

Insoluble poly basic salts of multivalent metals have shown a great promise in preparative reproducibility, ion exchange benaviour and both chemical and thermal stability. Many metals have been used for preparing materials such as aluminium, antimony, bismuth, cerium chromium, cobalt, iron, lead, magnesium, niobium, tin, tantalum, titanium, thorium, tungsten, uranium and zirconium. Also, a great number of anionic species have been used to form precipitates such as phosphate, tungstate, molybdate, arsenate, antimonate, silicate, tellurate, tellurite, ferrocyanide, vanadate, arseno-phosphate, arsenotungstate, arsenomolybdate, arseno-silicate, arsenovanadate, phosphotungstate, phospho-molybdate, phosphosilicate, phosphovanadate, molybdo-silicate and vanadosilicate. The work on these materials has been nicely summarized at different stages of its development by Clearfield (246), Amphlet (247) and Qureshi and Varshney (248).

Surface characterization and analytical applications are the two aspects in the study of inorganic ion exchangers. Surface characterization can be done in two ways:

a) By chemical methods and

b) By physical methods

The former methods include the composition, chemical and thermal stability and ion-exchange properties. A study of ion exchange properties takes into account the various characteristics of the material such as concentration and elution behaviour, ion-exchange capacity, pH-titration and distribution characteristics. Physical methods of characterization are X-ray diffraction, TGA/DTA and IR. They indicate the presence of certain ionogenic groups in the material, in addition to its crystalline nature. For amorphous inorganic ion exchangers, however, a great emphasis is given on the ion-exchange properties, followed by the physical characterization based on TGA/DTA and IR. A study of the analytical applications is important to explore the potential use of these materials.

As discussed earlier, inorganic ion exchangers have various applications in analytical chemistry owing to their resistance to heat and radiations. In addition to the ion-exchange procedures in which a high chemical and

thermal stability or a high selectivity for a particular ions are required, new applications are in the areas of heterogenous catalysis, solid electrolytes, inorganic ion-exchange membranes, ion-selective electrodes and intercalation compounds. In most of these fields, informations on ion exchange kinetics and mobility of counter ions in the lattice structure are needed. Similarly, ion exchange equilibria are of great practical and theoretical importance. The theoretical aspects of these two fundamental approaches have been discussed very well by Dyer (249) on zeolite models which appropriately reproduces the results on synthetic inorganic ion exchangers.

The theory of ion-exchange kinetics is not as far advanced as that of ion-exchange equilibria. The more recent quantitative approach to the ion-exchange equilibria include effects such as swelling pressure and specific interactions. The theory of ion-exchange kinetics, on the other hand, is still in the stage of first approximation. Kinetic studies answers some of the more interesting questions, namely:

i) What is the mechanism of ion-exchange ?

ii) What is the rate - determining step ?

iii) What rate laws are obeyed ?

Though many studies on the kinetics of ion-exchange on organic resins have been reported, relatively less informations exist on the kinetics of exchange on inorganic ion exchangers mainly because of their late developments. Probably, Nachod and Wood (250) have made the first serious attempt on the kinetic studies of ion-exchange. They studied the reaction rate with which the exchangeable ions are released from the exchanger. Boyd et al. (251) studied later on the kinetics of metal ions upon the resin beads and gave a clear picture of the particle and film diffusion phenomena governing the ion-exchange process. The former is valid at high concentrations while the latter at low concentrations. The kinetics of metal ions on sulphonated polystyrene was studied by Reichenberg (252) who also confirmed the above view. According to Nancollas (253) who studied the kinetics of Na(I)-H(I) exchange on crystalline zirconium phosphate, the rate of exchange is initially fast and then becomes slow. Fuga and Kikindi (254) studied the kinetics of ion-exchange of alkali metals on zirconium antimonate in hydrogen form at 25°C and found that the rate of reaction increases with the atomic number of the cation. Alberti et al. (255) observed that the rate of exchange decreases from Ba(II) to Sr(II) and that it is low perticularly for Mg(II) ion on

zirconium(IV) phosphate. Costantino (256) studied the self diffusion of Na(I) and K(I) on microcrystals of $Zr(NaPO_4)_2.3H_2O$ and $Zr(KPO_4)_2.3H_2O$ and modified the Fick's equation to take into account the nonuniformity of the particle size. The equation obtained has been employed in a study of the self-diffusion rate of Na(I) and K(I) in the above exchanger and the mobility data have been compared with the conductivity data available for the same ionic forms.

However, most of the studies (257-269), reported in literature, are based on the Bt criterion (251) which is of limited use because of the different mobilities (270) of the competing ions. This criterion is useful for ions having similar effective diffusion coefficients i.e. for an isotopic exchange process. In a true ion exchange phenomenon the fluxes of at least two different ionic species are coupled with one another. Thus, a single diffusion coefficient cannot describe the actual process. In such a case the non-linear Nernst-Planck equations (271,272) should be applicable for a particle diffusion controlled ion-exchange with some additional assumptions. For practical purposes,an explicit expression was given by Helfferich et al. (273,274) which approximates the numerical results. Varshney et al. (275-285)

and Bobman et al. (286) have conducted some studies based on this new criterion.

In all the calculations involving ion-exchange kinetics using the Nerst-Planck equations, evaluation of dimensionless time parameter (T) is a prerequisite. A graphical method is generally used for this purpose, which is tedious and gives only approximate T values resulting in the less accurate kinetic parameters. In view of this, exhaustive studies were made in these laboratories (287) in this direction. As a result T values were computed for the different mobility values of bivalent cations. These studies have now greatly simplified the most tedious procedure of finding the T values and are the landmark in this direction.

Thermodynamic studies are important to understand the behaviour of an ion exchanger and form the basis of an ion-exchange process. Thermodynamic predictions are easy on an inorganic ion exchanger because of its rigid matrix, accompanied with a negligible swelling. When an ion exchanger having a counter ion 'A' is placed in a solution of counter ion 'B', an equilibrium will eventually be set up between the exchanger and solution phases. This exchange

at equilibrium may be represented as:

$$\bar{A} + B(aq) \rightleftharpoons \bar{B} + A(aq)$$

Here the effect of coions may be considered negligible for the sake of simplicity..The thermodynamic equilibrium constant for the reaction may be written as:

$$K_a = \frac{\bar{a}_B \, a_A}{\bar{a}_A \, a_B}$$

An ion exchange equilibrium may be described by two different theoretical approaches. One is based on mass action law while the other is based on the Donnan theory. Donnan theory has an advantage of permitting a more elegant interpretation of the thermodynamic behaviour in an ion exchanger. However, mass action approach is straight forward and it gives a semiquantitative picture. Probably, the first quantitative information of ion-exchange equilibria was made by Gans (288) using the mass action law in its simplest form. A general treatment was given by Gaines and Thomas (289).

Free energy changes in the ion-exchange process can be calculated with the help of thermodynamic equilibrium constant. The free energy change of the system is important to know, by which one can estimate the preferential

uptake of the counter ions by the exchanger. The ionic selectivity is governed by the lowering of the free energy change of the ion exchange system and can be evaluated by knowing the K_a values at different temperatures.

Most of the thermodynamic studies have been done on alkali and alkaline earth metals. The ion exchange equilibria of alkali metal ions have been studied by Larsen and Vessers (290), and by Gal and Ruvarac (291) on zirconium phosphate of various composition and properties. Recently, extensive studies on ion exchange thermodynamics of alkali metal ions have been made with a more defined semi-crystalline and crystalline zirconium phosphate (292-302). Baestle (303) studied the exchange of Ca^{2+}, Sr^{2+}, Ce^{3+} and Eu^{3+} ions with hydrogen ions both at micro and macro concentration levels over a range of temperatures (5-70°C) on zirconium phosphate. The ion-exchange equilibrium studies Ca^{2+} - H^{+} (304) and UO_2^{2+}- H^{+} (305) have been made by Ruvarac on crystalline zirconium phosphate. The thermodynamic exchange on zeolite has been made to a greater extent. Barrer (306,307), Sherry (308,309) and Dyer (310) studied the effect of temperature with different zeolites in various cationic forms.

Similar studies have also been made on inorganic anion exchangers. The reversibility of Br^- - NO_3^- exchange on hydrous zirconia was demonstrated by Kraus (311). Thermodynamics of Cl^- - NO_3^-, Cl^- - SCN^- and SCN^- - Cl^- exchange on hydrous zirconium oxide was studied by Nancollas and Paterson(312).

Some of the equilibrium studies already made on different ion exchangers with various systems and their parameters are given in Table 1.1.

It is clear from the above survey that very few systematic studies have been reported on the adsorption behaviour of activated carbon for organic pollutants. Organic pollutants, containing a tertiary nitrogen, are the worst offenders to the environmental peace and ecological balance, as they are central nervous system (CNS) depressants and skin irritants. They cause respiratory tract and gastrointestinal disturbances, damage kidneys and liver and are suspected carcinogens. Organics containing a tertiary nitrogen group, add up to the environment as a result of degredation of prcteineous materials, industrial wastes and chemicals used in agricultural practices and are causing land, water and air pollution. In view of this the present work has been undertaken for a systematic. study of these compounds.

TABLE 1.1

Thermodynamic Studies made on various Ion Exchange Materials

lo.	Ion Exchange Material	Type of Material	Systems studied	Various Parameters studied	References
.	Zirconium phosphate	Crystalline	Na^+, Cs^+-H^+ exchange	Phases formed during the exchange at equilibrium	313
		Amorphous	UO_2^{2+}/H^+	K, $\triangle G^o$, $\triangle H^o$ and $\triangle S^o$	305
		Crystalline	K^+/H^+	$\triangle G^o$, $\triangle H^o$ and $\triangle S^o$	314
		Crystalline	Cs^+/H^+, Rb^+/H^+	Forward and Reverse isotherms X-ray diffractogram	315
		Semicrystalline	Li^+/H^+, K^+/H^+ and C_s^+/H^+	$\triangle G^o$, $\triangle H^o$ and $\triangle S^o$	316
		Semicrystalline	Cs^+/Rb^+ and Cs^+/K^+	K, $\triangle G^o$ and $\triangle H^o$	317
.	Antimonic acid	Crystalline	H^+/Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Ca^{2+}	ln K, $\triangle G^o$, $\triangle H^o$ and $\triangle S^o$	318
		Crystalline	Mg^{2+}/H^+, Ca^{2+}/H^+, Sr^{2+}/H^+ and Ba^{2+}/H^+	Selectivity sequence, reversibility, X-ray studies	319
		Crystalline	NH_4^+/H^+, $CH_3NH_3^+/H^+$, $C_2H_5NH_3^+/H^+$, $(CH_3)_2NH_2^+/H^+$, Iso-$C_3H_7NH_3^+/H^+$ and $(C_2H_5)_4N^+/H^+$	ln K, $\triangle G^o$, $\triangle H^o$ and $\triangle S^o$	320

(TABLE 1.1 CONTINUED)

3.	Ferric antimonate	Amorphous	$H^+/Li^+, Na^+, K^+$, and Rb^+	K, $\triangle G$, $\triangle H$ and $\triangle S$	321
		Amorphous	$Na^+/Ba^{2+}, Mg^{2+}, Ca^{2+}$ and Sr^{2+}	K, $\triangle G$, $\triangle H$ and $\triangle S$	322
4.	Niobium arsenate	Amorphous	$H^+/Na^+, K^+, Mg^{2+}, Ca^{2+}$, Ba^{2+} and Sr^{2+}	K_H^m, $\triangle G$, $\triangle S$, $\triangle H$ and S_{EX}	323
5.	Cerium phosphate	Amorphous	Li^+/H^+, Na^+/H^+, K^+/H^+	$\triangle H^o$	324
6.	Antimony silicate	Crystalline	Mg^{2+}-H^+, Ca^{2+}-H^+, Ba^{2+}-H^+	K, $\triangle G^o$, $\triangle H^o$, $\triangle S^o$, $\triangle G_M^x$ H_M^x and $\triangle S_M^x$	325,326
7.	Zirconium phosphosilicate	Amorphous	Mg^{2+}-H^+, Ca^{2+}-H^+, Ba^{2+}-H^+ and Sr^{2+}-H^+	K, $\triangle G^o$, $\triangle H^o$, $\triangle S^o$ $\triangle G_M^x$, $\triangle H_M^x$ and $\triangle S_M^x$	327,328
8.	Sodium polysilicate	-	H^+, Li^+ and K^+	$\triangle G$, $\triangle H$ and $\triangle S$	329
9.	Zeolites and Clay	Crystalline	Na^+ - Ca^{2+} exchange	Ion-exchange isotherms	330
10.	Zeolite RHO	Crystalline	-	Ion-exchange isotherms	331
11.	Synthetic faujasite	Crystalline	Li^+, K^+, Rb^+, Ce^+, Ag^+ and Tl^+	Ion-exchange isotherms and $\triangle G$	309
12.	Zeolites Na-X and Na-Y	Crystalline	Li^+, Na^+, K^+, Rb^+, Ca^{2+} Sr^{2+} and Ba^{2+}	$\triangle G$, $\triangle H$ and $\triangle S$	306

This study describes the adsorption of nicotinic acid and 2,6-lutidine on activated carbon. In addition to this the equilibrium studies of some heavy metal ions viz. Fe(III), Cu(II), Ni(II), Mn(II) and Hg(II) on the surface of antimony(V) arsenophosphate, an amorphous inorganic ion exchanger have also been made. Finally the dimensionless time parameter T has been evaluated for some particle diffusion controlled forward and reverse H(I)-Cation(I), OH(I)-Anion(I) and OH(I) - Anion(II) exchanges by using a computer programme. These T values simplify the treatment of kinetic parameters and improves the accuracy of results over the old graphical method.

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CHAPTER - II

ADSORPTION OF TERTIARY NITROGEN CONTAINING COMPOUNDS ON ACTIVATED CARBON:EQUILIBRIUM STUDIES OF NICOTINIC ACID IN AQUEOUS SYSTEMS

INTRODUCTION

Pollution is now an important problem owing to increased industrialization and population overflow, and much effort is directed towards its control. Use of adsorbents, particularly activated carbon, is of current interest in the removal of pollutants from air and water. The U.S. and Netherlands waterworks associations have reported the use of activated carbon for the removal of volatile organic compounds from drinking water (1). Recently, Nishino and Nakano (2) have reviewed the role of activated carbon for water and wastewater treatment, while Shelygin and Korol'kov (3) reviewed adsorption for the removal of pollutants from waste gases. Removal of chlorohydrocarbons from water by ozonation and extended granular activated carbon adsorption was reported by Awazi (4). Sander (5) reported the use of a granular carbon filter for the purification of drinking water from organic contaminants and NH_4^+. Lulek and Grochmalicka-Mikolajczyk (6) removed organic substances from water by passing it through activated carbon. They also analyzed the adsorption isotherms of phenol, indole and lauryl sulphate on different types of carbons. Various other studies have been conducted to examine the static and dynamic adsorption behaviour of activated carbon towards pollutants in the treatment of water and wastewater (7-10).

The use of activated carbon has also been reported in the adsorption of hydrocarbons (11), phenols (12), alcohols (13), organic acids (14), dyes (15), pesticides (16) and pollutants (17).

The present work aims to study the adsorption behaviour of activated carbon for nicotinic acid, a tertiary nitrogen-containing compound. Such compounds are suspected to have carcinogenic behaviour, and hence their systematic study might reveal interesting results. The adsorption studies have been made in two media, namely pure water and NaCl solution, at different temperatures. The appropriate thermodynamic parameters have also been calculated and are discussed.

EXPERIMENTAL

Reagents and chemicals

Activated carbon No E4 34011was obtained from E. Merck (India) Ltd. Nicotinic acid was obtained from E. Merck (F.R.G.). All other reagents used were of analytical grade.

Apparatus

A water-bath incubator-shaker having a temperature variation of $\pm 0.5^{\circ}C$ was used for the equilibrium studies.

Preliminary treatment of activated carbon (AC)

The AC was used after drying at $105^{\circ}C$ for 2 h. It was purified (18) by stirring in 1 M hydrochloric acid for 3 h, filtering, and washing with distilled water until it was free from chloride ions. Finally it was dried at $105^{\circ}C$. The dried AC was then kept in a Soxhlet apparatus for about 10 days before being stored in a dessicator over anhydrous P_2O_5.

Solution of nicotinic acid (NA)

A stock solution of 0.1 M NA was prepared in distilled water. Different volumes of the stock solution

were added to give the required concentration of NA in the equilibrating solution. The error analysis in the concentration determination for nicotinic acid is summarized in Table 2.1.

Adsorption studies

Samples weighing 0.5 g of the purified AC were shaken with 50 ml NA solutions of different concentrations at 30, 40, 50 and 60°C for 72 h. Preliminary studies have shown that equilibrium is reached within this period. The adsorption was studied in pure aqueous and 0.1 M NaCl media.

After 72 h the equilibrating solutions were filtered and titrated against a standard NaOH solution using phenolphthaline as an indicator to determine the equilibrium concentration (C_e) of NA in the solutions. The amount of NA in mmol g^{-1} AC (A_m) was calculated from the difference of NA added (C_i) and the concentration of NA in mmoll^{-1} (C_e) in the solution after equilibrium.

Treatment of data

(a) To determine the isotherm shapes, A_m values were plotted as a function of C_e at different temperature for both the systems. The plots are shown in Fig. 2.1.

TABLE 2.1

Error analysis in the concentration determination of nicotinic acid (true value = 0.100 M NA)

Sample No.	Observed value (mol l^{-1})	Absolute error	Relative error (%)
1	0.1030	0.0030	3.0
2	0.1034	0.0034	3.4
3	0.1040	0.0040	4.0
4	0.1032	0.0032	3.2

Standard deviation (S.D.) = 4.3205×10^{-4}

Coefficient of variation = 0.4178

S.D. (mean) = 2.1602×10^{-4}

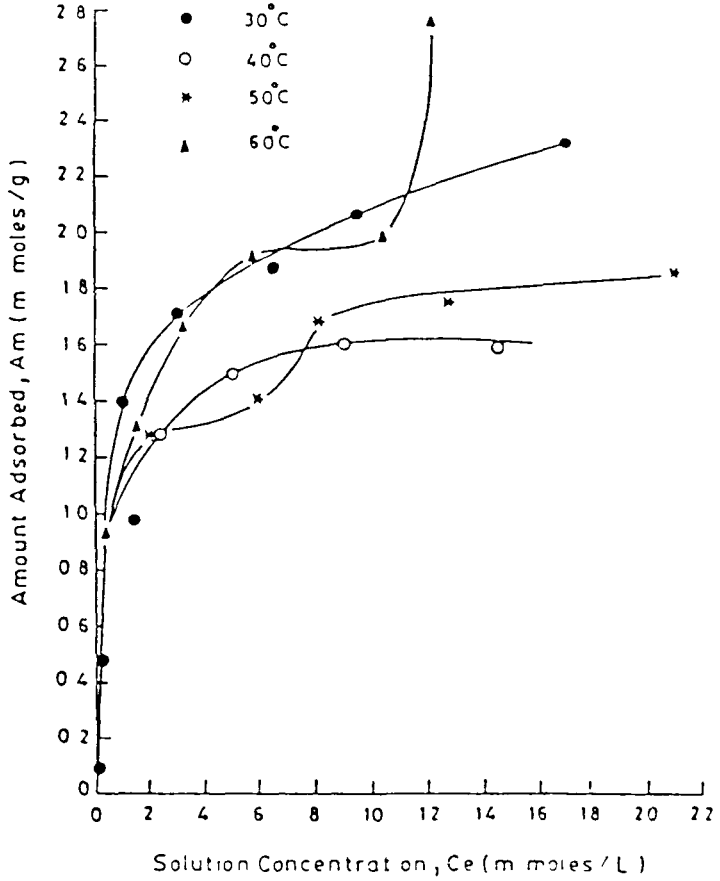

Fig. 2.1(a): THE ADSORPTION OF NICOTINIC ACID ON ACTIVATED CARBON AT DIFFERENT TEMPERATURES IN PURE AQUEOUS MEDIUM.

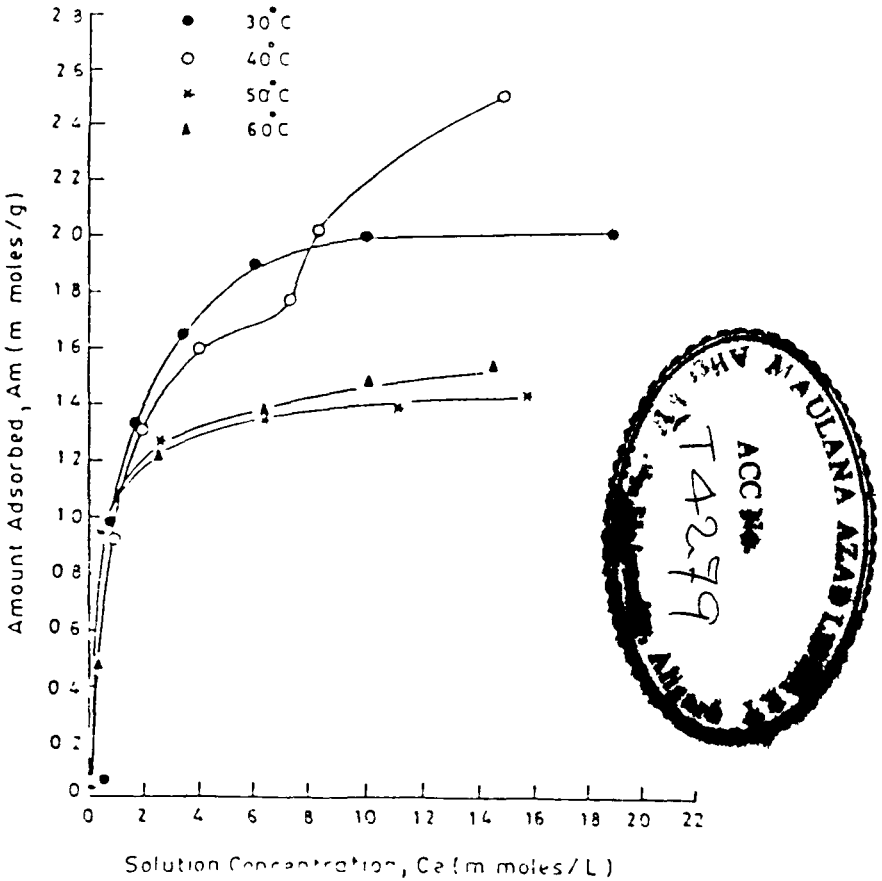

Fig. 2.1(b): THE ADSORPTION OF NICOTINIC ACID ON ACTIVATED CARBON AT DIFFERENT TEMPERATURES IN 0.1M NaCl MEDIUM

(b) A computer simulation technique was used to fit the adsorption data for the following adsorption models:

(i) Langmuir model: According to this model

$$C_e/A_m = \frac{1}{K} \cdot \frac{1}{b} + \frac{1}{b} \cdot C_e \qquad \ldots\ldots (1)$$

where C_e and A_m are as mentioned earlier. K is the equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence a plot of C_e/A_m versus C_e should give a straight line with a slope 1/b and an intercept 1/Kb as shown in Fig. 2.2.

(ii) Freundlich model: According to this model

$$\ln A_m = \ln K + \frac{1}{n} \ln C_e \qquad \ldots\ldots (2)$$

where all the terms have the usual significance and n is an empirical constant. Thus a plot of $\ln A_m$ versus $\ln C_e$ should give a straight line with slope 1/n and intercept $\ln K$.

(c) Thermodynamic parameters $\ln K$, $\triangle G$, $\triangle S$ and $\triangle H$ were calculated from the equations given below.

The free energy change ($\triangle G$) was calculated from the relation

$$\triangle G = - RT \ln K \qquad \ldots\ldots (3)$$

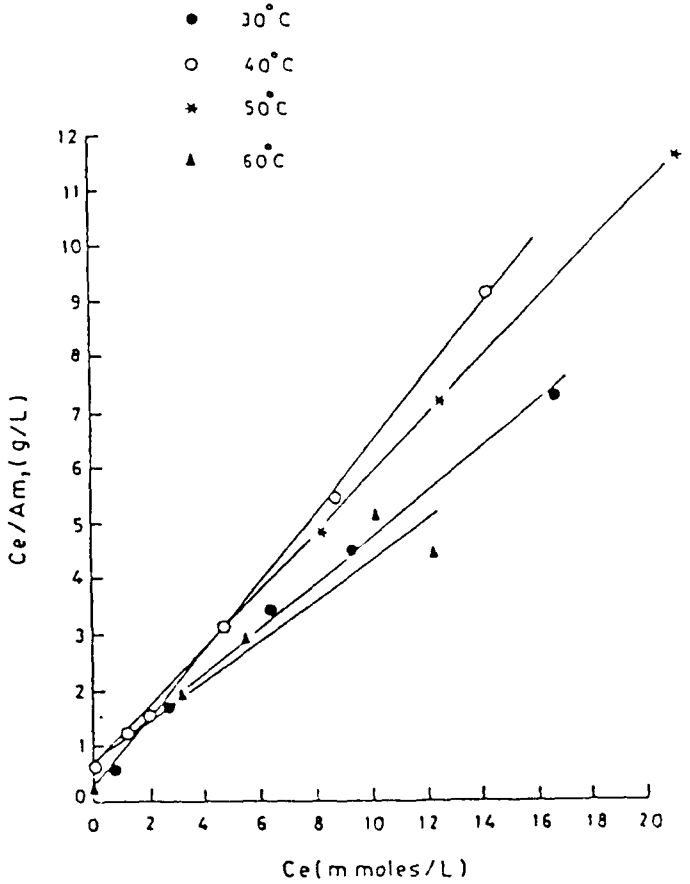

Fig. 2.2(a): LANGMUIR PLOTS FOR THE ADSORPTION OF NICOTINIC ACID ON ACTIVATED CARBON IN PURE AQUEOUS MEDIUM.

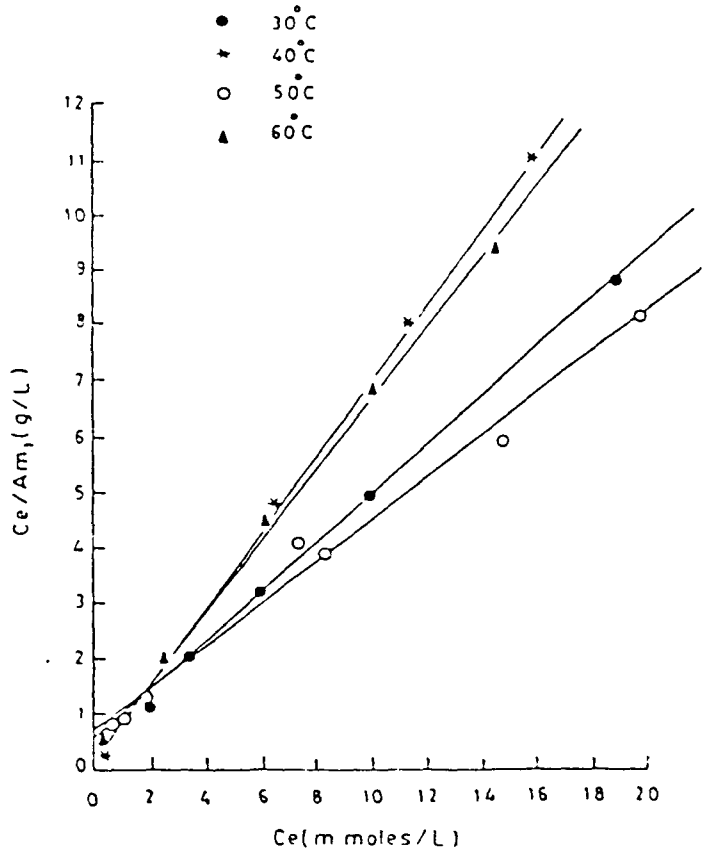

Fig.2.2(b): LANGMUIR PLOTS FOR THE ADSORPTION OF NICOTINIC ACID ON ACTIVATED CARBON IN 0.1M NaCl MEDIUM.

Similarly the enthalpy change ($\triangle$ H) between 30 and 60^{o}C was calculated from the following equation:

$$\ln K = \frac{-\triangle H}{RT} + C \qquad \ldots\ldots (4)$$

and the entropy change ($\triangle$ S) was calculated from the equation

$$\triangle G = \triangle H - T \triangle S \qquad \ldots\ldots (5)$$

RESULTS AND DISCUSSION

The adsorption of nicotinic acid (NA) on activated carbon (AC) has been studied at 30, 40, 50 and 60°C in the following media:

(1) pure water and

(2) 0.1 M NaCl solution

All the isotherms (Fig. 2.1) follow a Langmuirian pattern, as is evident on comparing the coefficients of determination of least-squares fitting (r) shown in Table 2.2. Most of the isotherm belong to the L_2 type and are sigmoid, except the isotherms at 40°C, in the presence of NaCl, which is of the L_4 type (19). The adsorption isotherm at 60°C shows a steep rise in adsorption isotherm at $C_e > 10$ mmol l^{-1}. The adsorption of NA does not show a regularly increasing or decreasing trend in any of these systems over the temperature range studied. With an increase in the concentration of NA in the solution phase the adsorption increases, and a cross-over of the adsorption isotherms occurs in a complex manner in both media. As the plots of maximum adsorption (A_m) against temperature at different critical equilibrium concentrations suggest (Fig. 2.3), the maximum adsorption (2.76 mmol g^{-1}) is obtained at 60°C at $C_e > 10$ mmol l^{-1} in the pure aqueous system. However, in the presence of

TABLE 2.2

Statistical parameters (r, 1/n, 1/b) for the Freundlich and Langmuir isotherms for the adsorption of nicotinic acid on AC in pure water and 0.1 M NaCl systems

T (°C)	Pure aqueous medium				0.1 M NaCl medium			
	Freundlich isotherm		Langmuir isotherm		Freundlich isotherm		Langmuir isotherm	
	r	1/n	r	1/b	r	1/n	r	1/b
30	0.8862	0.4831	0.9939[a]	0.7715	0.8821	0.4831	0.9999[a]	0.1806
40	0.9549	0.2527	0.9995[a]	0.6134	0.9549	0.2527	0.9833[a]	0.3774
50	0.6380	0.4005	0.9969[a]	0.5261	0.8638	0.4005	0.9992[a]	0.6850
60	0.9598	0.3359	0.9659[a]	0.3824	0.9598	0.3359	0.9987[a]	0.6434

[a]These r values represent the best fitting of each type of adsorption isotherm.

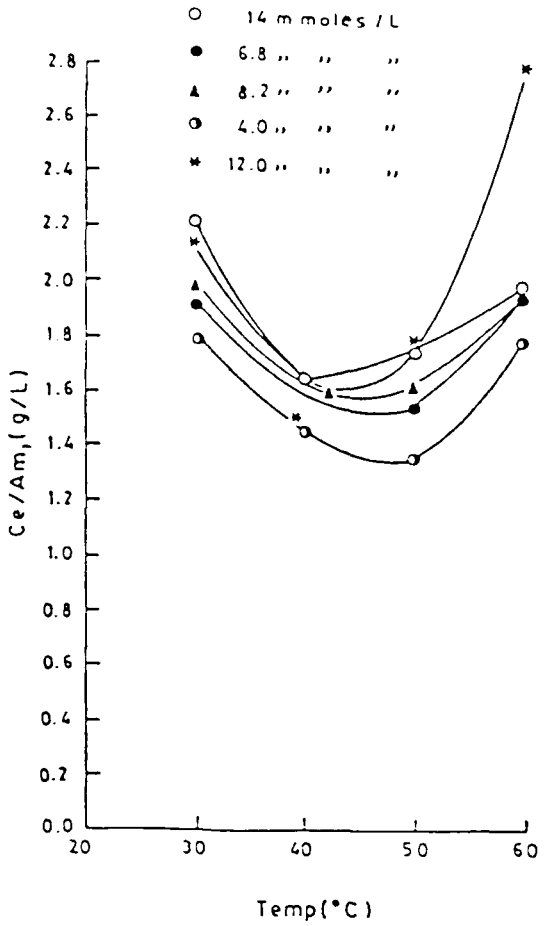

Fig. 2.3(a): THE MAXIMUM ADSORPTION ACHIEVED WITH TEMPERATURE AT DIFFERENT CRITICAL EQUILIBRIUM CONCENTRATIONS IN PURE AQUEOUS MEDIUM.

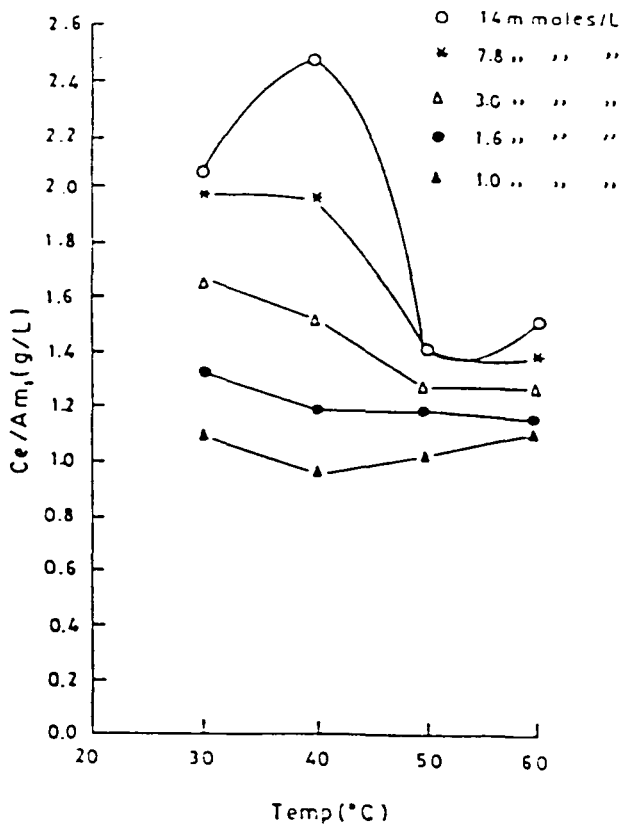

Fig.2.3(b): THE MAXIMUM ADSORPTION ACHIEVED WITH TEMPERATURE AT DIFFERENT CRITICAL EQUILIBRIUM CONCENTRATIONS IN 0.1 M NaCl MEDIUM.

NaCl the maximum adsorption (2.4 mmol g^{-1}) is observed at 40°C at $C_e > 14$ mmol l^{-1}. Thus, in the presence of NaCl at 40°C and in its absence at 60°C the isotherms show unique behaviour, which may be interpreted in terms of the different types of arrangement of NA molecules at the surface of the AC. The shapes of the isotherms and the enthalpy data indicate that the adsoprtion of NA on the AC is due to physisorption (20).

The plateaus are obtained in the absorption isotherms at 50°C in NaCl solution and at 40°C in pure water owing to the formation of a complete monolayer of NA on the surface of the AC. The maximum slope in the NaCl medium was found to be 0.68 at 50°C, and in the pure aqueous medium at 40°C it was 0.61. We calculated the amount of NA needed to form a monolayer on AC (b) corresponding to these values. Thus we get b = 1.47 mmol g^{-1} at 50°C in presence of NaCl and b = 1.64 mmol g^{-1} at 40°C in its absence. Thus an average of about 1.56 mmol g^{-1} of NA is needed to form a complete monolayer on the surface of the AC.

A critical analysis of the adsorption isotherm in the pure aqueous system reveals that the adsorption of NA on the AC increases with a rise in temperature from 40 to 60°C. The total adsorption at 30°C shows an

abnormal value, i.e., between 50 and 60°C. This anomaly may be interpreted in terms of an increased adsorbate-adsorbent interaction, i.e. strong hydrogen bonding between the functional groups of NA and that of the AC. A steep rise in the adsorption isotherm at 60°C above $C_e > 10$ mmol l^{-1} is observed. This may be due to the condensation of NA molecules on the AC surface (21). With the rise in temperature the carboxylic groups of NA are desolvated, making it less hydrophilic and more compact, which increases the surface activity and saturation value. Because of the increase in compactness (i.e. a decrease in the effective surface of the adsorbate) with the rise in temperature, adsorption increases between 40 and 60°C, and finally a capillary condensation effect is seen at 60°C (22).

The adsorption isotherms in the presence of NaCl show a pattern that is quite different from those of the aqueous medium. Here, the adsorption process may be divided into two groups, first the group at 30 and 40°C, and secondly those at 50 and 60°C. In both groups the total adsorption increases with the rise in temperature independently, as discussed earlier. The reason for a completely different trend in this system from that of the pure aqueous one can be explained as follows:

1. Activation of the AC surface in the presence of NaCl by the removal of oxygenated complexes from the surface and
2. A decrease in the hydrogen bonding between the functional groups of NA and that of AC due to the salt formation on these groups.

The fact that the presence of NaCl decreases the adsorption of NA at 30°C (as compared with the pure aqueous system) might be due to a slight decrease in hydrogen bonding. There is an marked increase in the adsorption of NA. This may be due to the removal of oxygenated complexes from the surface, and hence an increase in the adsorption at this temperature is probably due to a change in the orientation of NA molecules (from parallel to perpendicular to the surface of AC), leading to a partially pore-filling nature (23).

A decrease in the adsorption of group II of the NaCl medium may be interpreted in terms of a large decrease in hydrogen bonding. This change in the adsorption pattern may be due to desolvation of the functional group of the AC at elevated temperatures (50 and 60°C) and, further, salt formation between the functional groups present on the surface and the adsorbate molecules.

Thus salt formation enhances the solvation of functional groups, resulting in a decrease in the compactness of the adsorbate molecules (NA), thereby causing a decrease in adsorption.

The adsorption processes in both systems follow a reverse trend between 30 and 40°C, and a similar trend between 50 and 60°C. At 30 and 60°C, in the simple system the extents of adsorption are almost same, but in the NaCl system they are quite different.

The thermodynamic parameters (ln K, $\triangle$ G and $\triangle$S) for the two systems are plotted as a function of temperature in Fig. 2.4. It is interesting to note from these data that the ordering of the adsorbed NA molecules on the AC decreases with increasing temperature between 30 and 40°C in the pure aqueous medium but that it increases between 40 and 60°C in presence of NaCl. Thus the ordering of NA molecules becomes equal at 30 and 60°C. The molecules become perpendicular (in a highly disordered manner) to the surface at 40°C, and this results in the highest adsorption of NA. Since the overall process is exothermic (Table 2.3), an increase in temperature is unfavourable for adsorption in such a case.

The presence of NaCl makes the process endothermic. The effect of NaCl is evident in the entropy data, which

TABLE 2.3

Thermodynamic parameters at different temperatures for the adsorption of nicotinic acid

T (^{o}C)	Pure aqueous medium[a]			0.1 M NaCl medium[b]		
	ln K	$\triangle$G (kJ mol^{-1})	$\triangle$S (kJ mol^{-1}K^{-1})	ln K	$\triangle$G (kJ mol^{-1})	$\triangle$S (kJ mol^{-1}K^{-1})
30	-0.3403	0.8572	-0.0250	-0.1616	0.4071	0.1325
40	0.9580	-2.4931	-0.0135	-0.6121	1.5927	0.1283
50	-0.0051	0.0137	-0.0208	0.8128	-2.1828	0.1360
60	-0.3210	0.8889	-0.0228	1.0381	-2.8741	0.1340

[a] $\triangle$H = -6.7257 kJ mol^{-1}.

[b] $\triangle$H = 41.7477 kJ mol^{-1}.

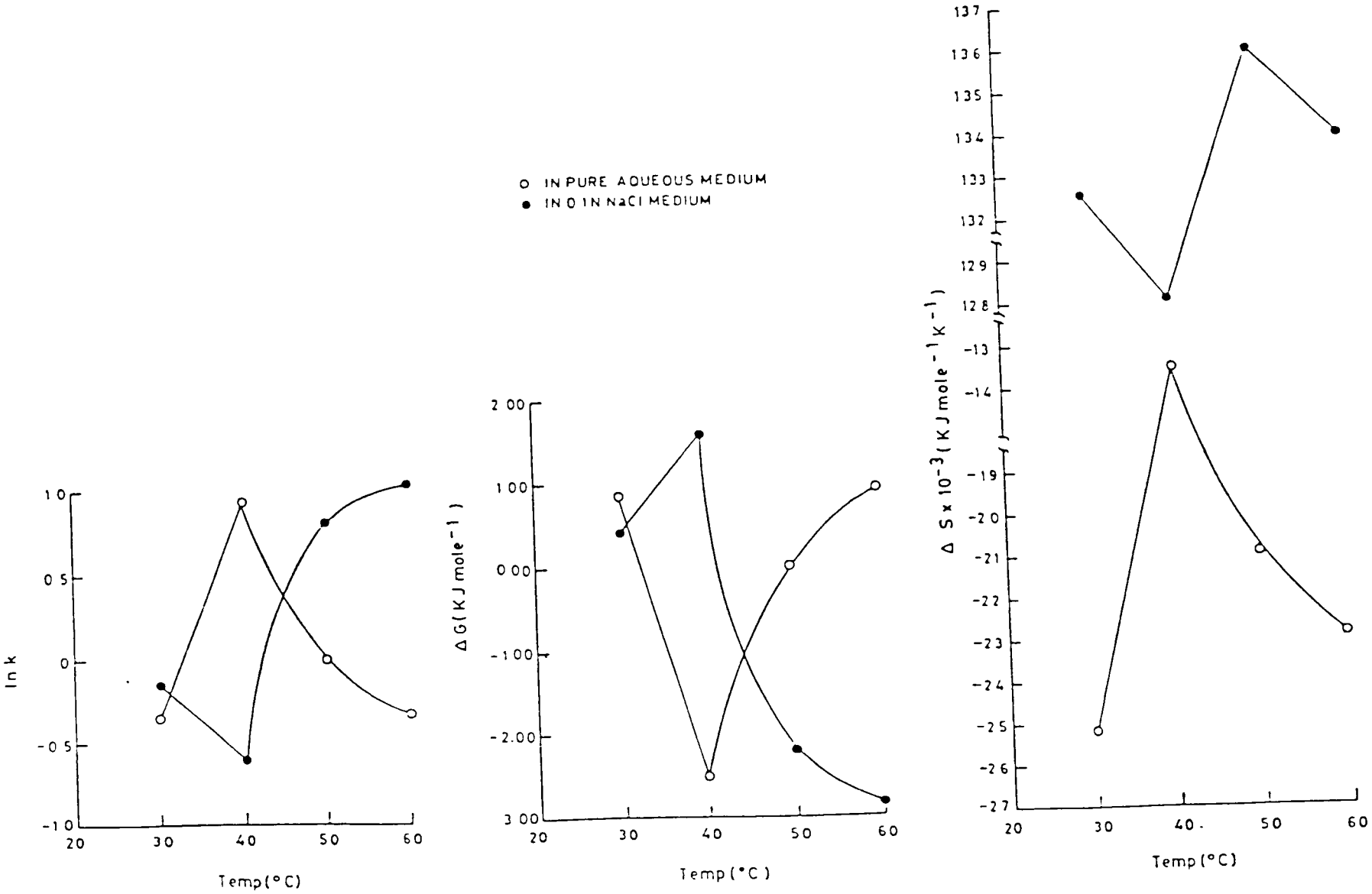

Fig. 2.4 : THE PLOTS OF THERMODYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES.

lie above tne level attained at any temperature in the pure aqueous system. This shows that in the presence of NaCl the molecules are more compactly arranged on the surface of the AC than in its absence. In this sytem the entropy decreases from 30 to 40°C and from 50 to 60°C independently, reaching the highest value at 50°C. The pattern is similar to the adsorption data shown in Fig. 2.1 and discussed earlier. At 40°C the $\triangle$ S value is a minimum which is very close to but higher than the value of $\triangle$ S obtained in the pure aqueous medium at this temperature. This further suggests that the NA/AC system in NaCl medium at 40°C is the most stable system and shows the highest A_m value. Further, the presence of NaCl enhances the adsorption capacity as well as the stability of the system, probably due to:

1. The increase in physical forces
2. The decrease in nicotinic acid-solvent interactions and
3. A perpendicular arrangement of the molecules on the surface of the AC.

With the rise in temperature, the increase in both A_m and the entropy may be due to the increased desolvation of -COOH groups of adsorbate and hence a more compact arrangement of NA molecules. These findings

forecast the good potential for activated carbon in wastewater treatment to remove these types of pollutants, particularly in the presence of NaCl and at moderate temperatures ($40^{o}C$).

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CHAPTER - III

ADSORPTION OF TERTIARY NITROGEN CONTAINING COMPOUNDS ON ACTIVATED CARBON:EQUILIBRIUM STUDIES OF 2,6-LUTDINE IN AQUEOUS SYSTEMS

INTRODUCTION

The principle objective of this investigation is to understand the surface reactions affecting the adsorption of some tertiary nitrogen containing compounds, present in the environment as pollutants, on the surface of activated carbon (AC). As a systematic study, two extreme cases namely an acid (Nicotinic acid) and a base (2,6-Lutidine or 2,6-Dimethylpyridine, DMP) have been selected. Which might reflect the nature of adsorbate-adsorbent interactions in such a system. In chapter II, the adsorption behaviour of nicotinic acid towards AC has been studied. Here, the adsorption behaviour of DMP on AC has been described.

The present study deals with the results obtained by the adsorption of DMP on the surface of AC. Different equations for different adosrption isotherms have been tried in order to fit the adsorption data by using a computer simulation technique. The overall thermodynamic parameters have been calculated on the basis of isosteric enthalpy at a particular surface coverage. A mechanism of adsorption is proposed in order to understand this adsorption process.

EXPERIMENTAL

Reagents and chemicals

Activated carbon No E4 34011 was obtained from E. Merck (India) Ltd. 2,6-Dimethylpyridine (DMP) was obtained from Sigma (U.S.A.). All other reagents and chemicals were of analytical grade.

Apparatus

A water-bath incubator shaker having a temperature variation of $\pm 0.5^{\circ}C$ was used for the equilibrium studies.

Preliminary treatment of the activated carbon (AC)

The AC was used after drying at $105^{\circ}C$ for 2h. It was purified (1) by stirring in 1 M hydrochloric acid for 3 h, filtering and washing with distilled water until it was free from chloride ions. Finally it was dried at $105^{\circ}C$. The dried AC was then kept in a Soxhlet apparatus for about 10 days before being stored in a dessicator over anhydrous P_2O_5.

Solution of 2,6-lutidine (DMP)

A stock solution of 0.1 M DMP was prepared in distilled water. Different volumes of stock solution were

added to give the required concentration of DMP in the equilibrating solution. The error analysis in the concentration determination for DMP is summarized in Table 3.1.

Adsorption studies

Samples of 0.5 g of the purified AC were shaken with 50 ml DMP solutions of different concentrations at 30, 40, 50 and 60°C for 72 h. Preliminary studies have shown that equilibrium is reached within this period. The adsorption was studied in a pure aqueous medium and in 0.1 M NaCl.

After 72 h the equilibrating solutions were filtered and titrated against a standard HCl solution using methyl orange as an indicator in order to determine the equilibrium concentration (C_e) of DMP in the solutions. The amount of DMP in mmol g^{-1} AC(A_m) was calculated from the difference of DMP added (C_i) and the concentration of DMP in mmol l^{-1} (C_e) in the solution after equilibrium. The plots are shown in Fig. 3.1.

Treatment of data

The treatment of data has been the same as described in chapter II. The thermodynamic parameters were obtained as follows:

TABLE 3.1

Error analysis in the concentration determination of 2,6-lutidine (true value = 0.100 M DMP)

Sample No.	Observed value (mol l^{-1})	Absolute error	Relative error (%)
1.	0.0985	-0.0015	-1.5
2.	0.0966	-0.0034	-3.4
3.	0.0986	-0.0014	-1.4
4.	0.0964	-0.0036	-3.6

Standard deviation (S.D.) = 1.187×10^{-3}

Coefficient of variation = 1.217

S.D. (mean) = 5.935×10^{-4}

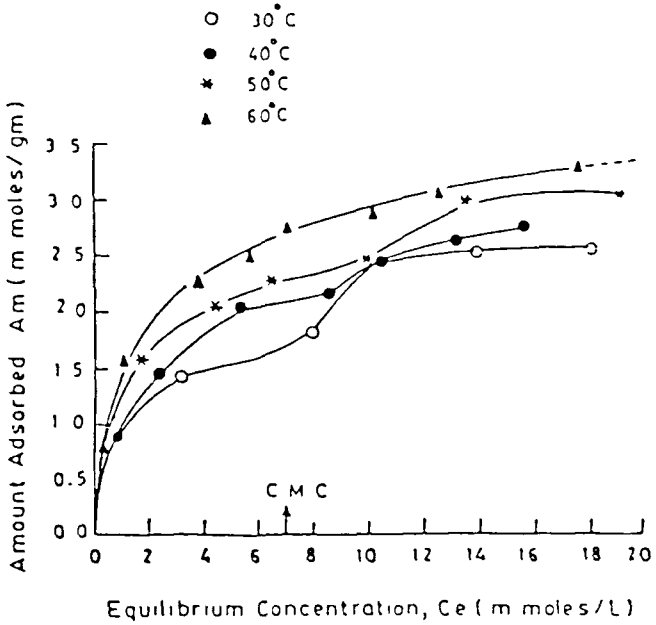

Fig. 3.1(a): THE ADSORPTION OF 2,5-LUTIDINE ON ACTIVATED CARBON AT DIFFERENT TEMPERATURES IN PURE AQUEOUS MEDIUM.

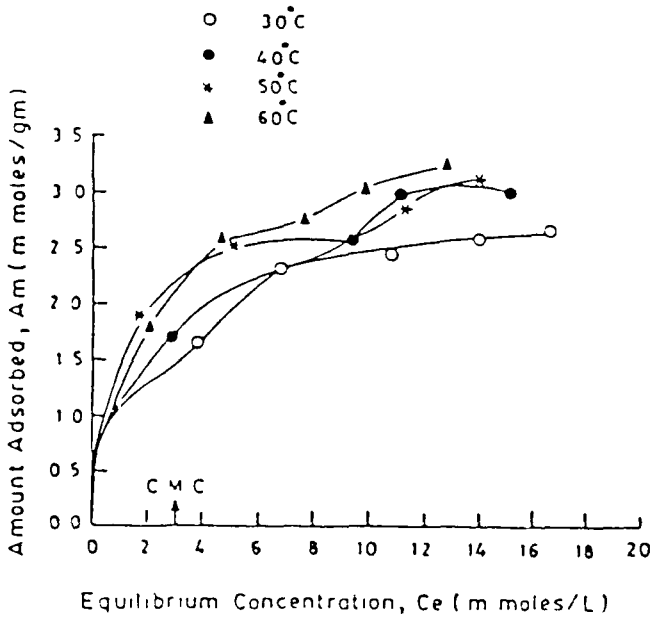

Fig.3.1(b) THE ADSORPTION OF 2,6-LUTIDINE ON ACTIVATED CARBON AT DIFFERENT TEMPERATURES IN 0.1 M NaCl MEDIUM

The free energy change ($\triangle G_m$) was calculated on the basis of the equilibrium concentration at a particular surface coverage of adsorption (2)

$$\triangle G_m = - RT \ln C_e \qquad \ldots\ldots\ldots (1)$$

Similarly the isosteric enthalpy ($\triangle H_m^{ads}$) was calculated by

$$\frac{\partial \ln C_e}{\partial T} \quad \frac{- \triangle H_m^{des}}{RT^2} \quad \frac{\triangle H_m^{ads}}{RT^2}$$

and the entropy change ($\triangle S_m$) was calculated by using the equation

$$\triangle G_m = \triangle H_m^{ads} - T \triangle S_m$$

RESULTS AND DISCUSSION

The analysis of the DMP absorption data reveals some interesting features. They follow a mixed trend in the adsorption pattern. Some obey Freundlich-type adsorption behaviour and other the Langmuir type. Table 3.2 summarizes these trends and compares the coefficients of determination of least-squares fitting (r) obtained from a computer analysis of the data. Plots for the Langmuir and Freundlich isotherms are shown in Fig. 3.2 and 3.3 respectively.

The adsorption process of DMP on AC in aqueous media in the presence or absence of NaCl can be explained on the basis of the following points:

1. Effect of equilibrium concentration
2. Effect of temperature and
3. Presence of an electrolyte.

The extent of adsorption in all these system increases with the increase in equilibrium concentration, as shown in Fig. 3.1. All the adsorption isotherms show two plateaus, except that obtained in water at $60^{o}C$. The first plateau in the isotherm occurs because of the adsorption of adsorbate molecule through the weak dispersive forces

TABLE 3.2

Statistical parameters (r, 1/n, 1/b) for the Freundlich and Langmuir isotherms for the adsorption of 2,6-lutidine on AC in pure water and 0.1 M NaCl systems

T (^{o}C)	Pure aqueous medium				0.1 M NaCl medium			
	Freundich isotherm		Langmuir isotherm		Freundlich isotherm		Langmuir isotherm	
	r	1/n	r	1/b	r	1/n	r	1/b
30	0.9852[a]	0.3351	0.9810	0.3454	0.9884	0.3040	0.9941[a]	0.3431
40	0.9947[a]	0.3563	0.9910	0.3261	0.9960[a]	0.3769	0.9935	0.2959
50	0.9940[a]	0.3396	0.9984	0.2960	0.9657	0.3466	0.9951[a]	0.3029
60	0.9926	0.3412	0.9965[a]	0.2849	0.9946	0.3579	0.9957[a]	0.2809

[a]These r values represent the best fitting of each type of adsorption isotherm

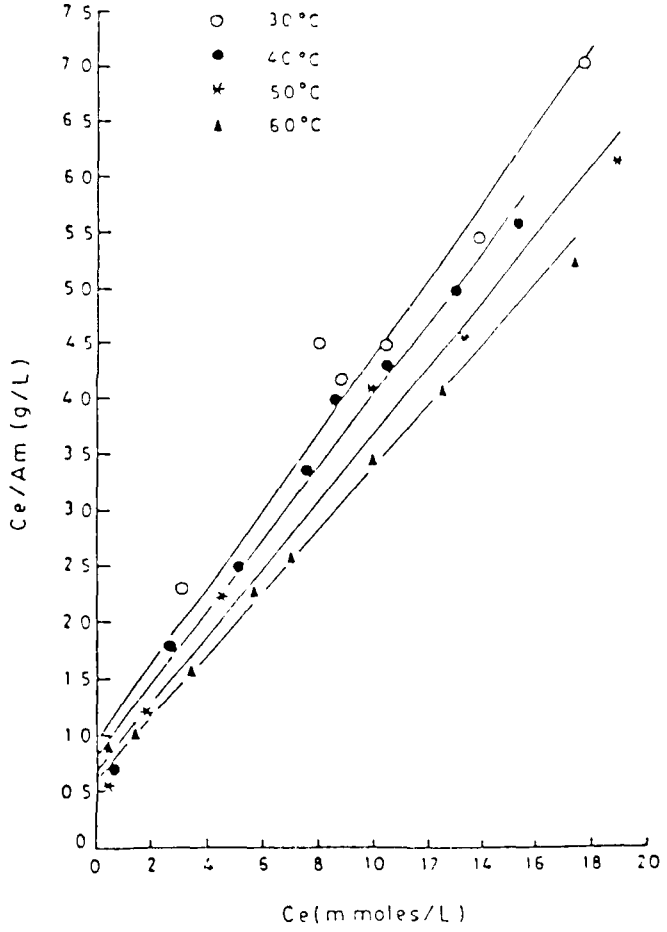

Fig.3.2(a): LANGMUIR PLOTS FOR THE ADSORPTION OF 2,6-LUTIDINE (DMP) ON ACTIVATED CARBON IN PURE AQUEOUS MEDIUM.

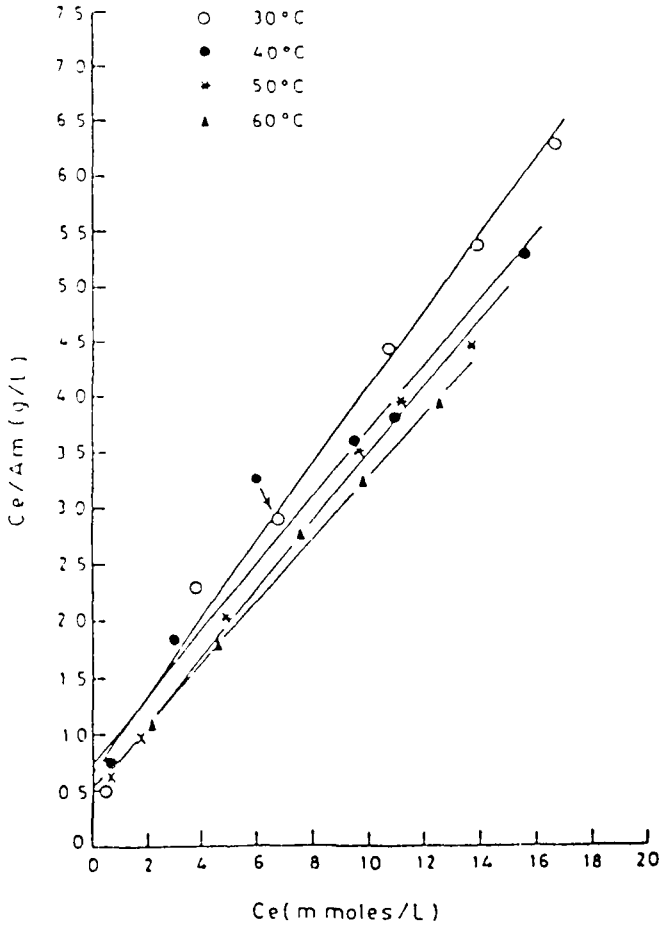

Fig.3.2(b): LANGMUIR PLOTS FOR THE ADSORPTION OF 2,6-LUTIDINE (DMP) ON ACTIVATED CARBON IN 0.1M NaCl MEDIUM

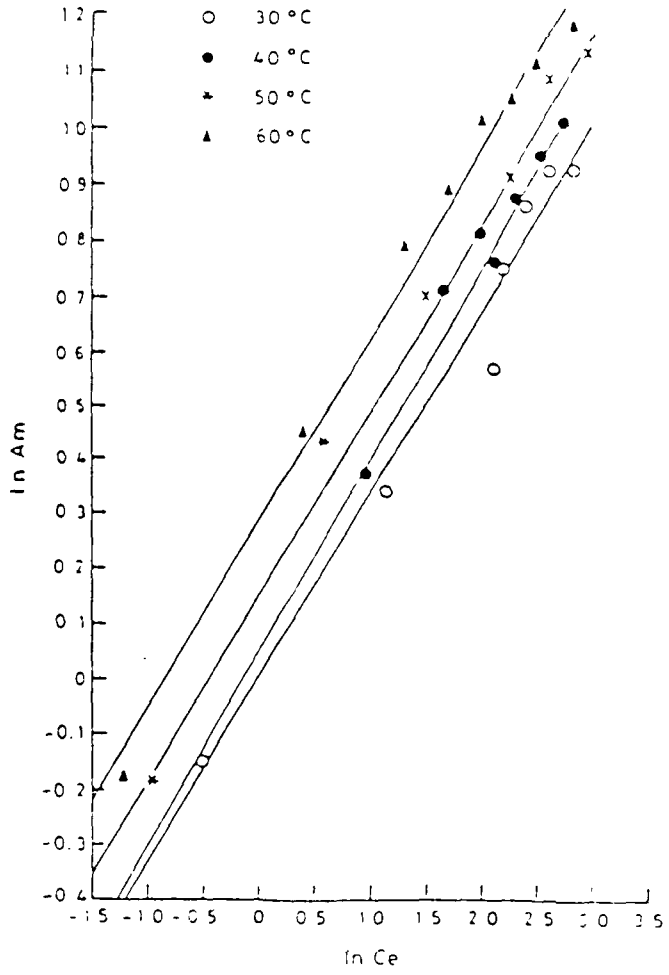

Fig.3.3(a): FREUNDLICH PLOTS FOR THE ADSORPTION OF 2,6-LUTIDINE (DMP) ON ACTIVATED CARBON IN PURE AQUEOUS MEDIUM.

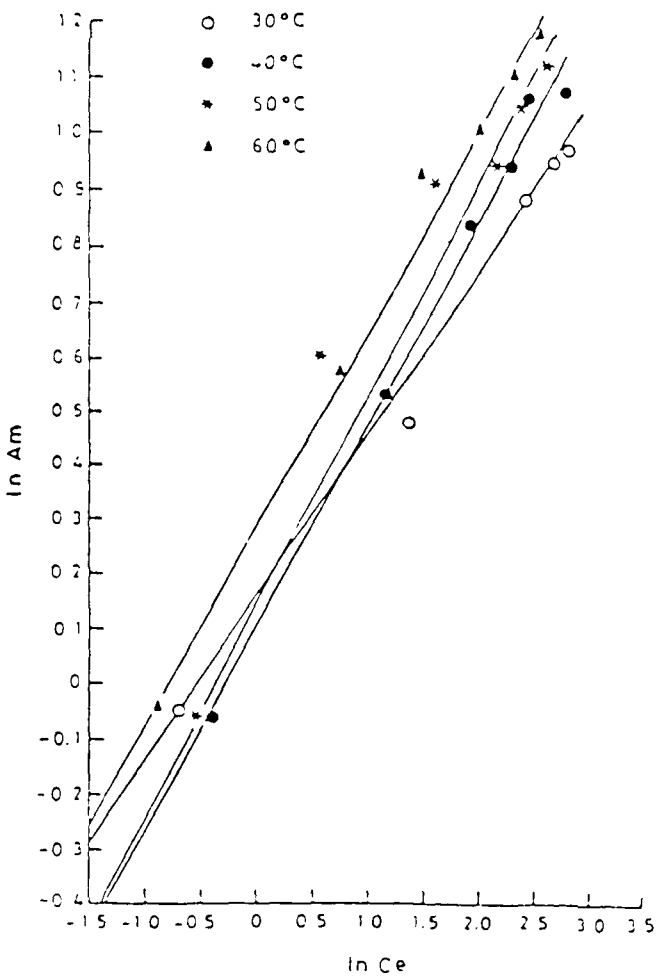

Fig.3.3 (b): FREUNDLICH PLOTS FOR THE ADSORPTION OF 2,6-LUTIDINE (DMP) ON ACTIVATED CARBON IN 0.1M NaCl MEDIUM.

(van der Waals forces) resulting from the hydrophobic part of the surfactant. The curve below the plateau represents the first stage of adsorption. At this stage, DMP molecules tend to lie flat on the surface of the AC, forming a monolayer which is shown in Fig. 3.4. By the time the monolayer is complete, most of the "free" solvent molecules are displaced from the surface of the AC and DMP should be hydrated. Hence there will be a continuous layer of solvated molecules in the interfacial layer of the AC (3). The increase in temperature has a positive role in the extent of adsorption in the systems studied. This effect may be interpreted in the light of desolvation, which with a rise in temperature, reduces the effective size of the adsorbate molecules and hence increases the adsorption (4,5).

In the subsequent stages, adsorption increases mainly through adsorbate-adsorbent interactions that initially determine how the adsorption proceeds when the first plateau is observed. These interactions mainly depend upon the nature of the adsorbent and on the hydrophilic-lipophilic balance in the surfactant. In case of NaCl solution at $30^{\circ}C$, the point of inflection is observed earlier in the isotherm as compared to the

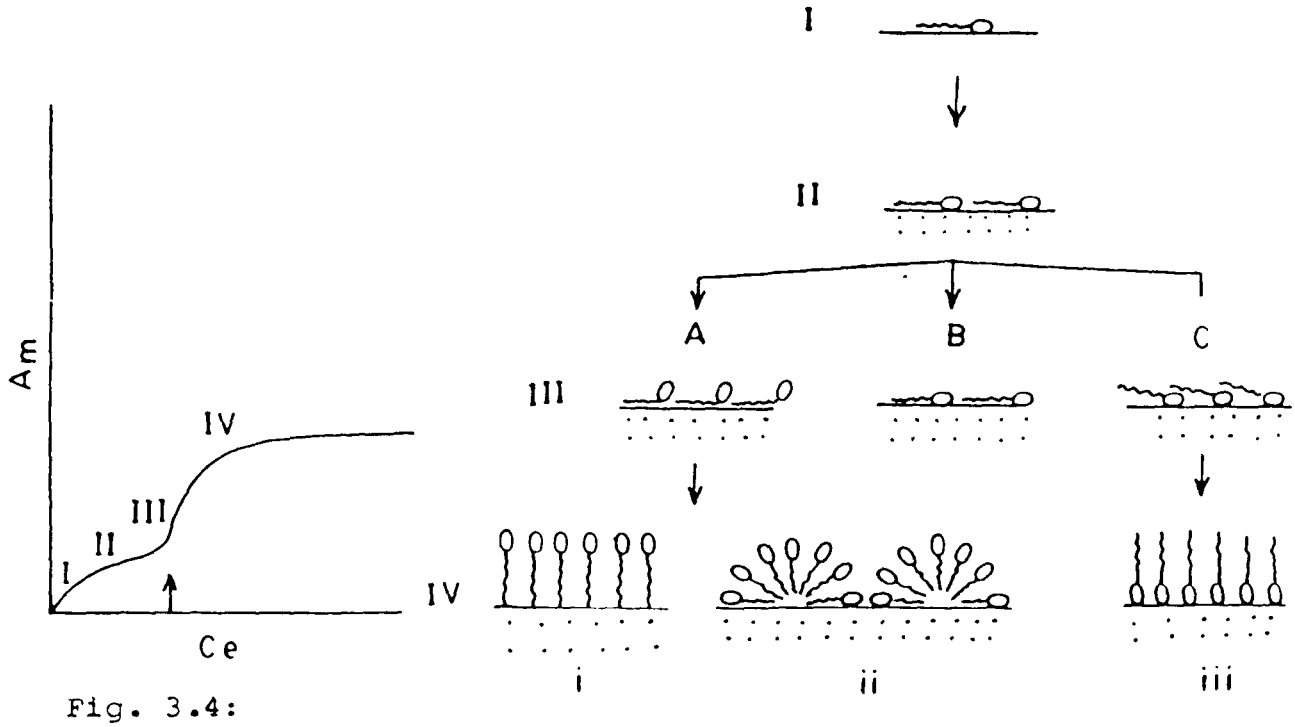

Fig. 3.4:

MODEL FOR THE ADSORPTION OF 2,6-LUTIDINE (DMP) ON ACTIVATED CARBON, SHOWING THE ORIENTATION OF DMP MOLECULES AT THE SURFACE. I-IV ARE THE SUCCESSIVE STAGES OF ADSORPTION AND SEQUENCES A-C CORRESPOND TO SITUATIONS WHERE THERE ARE RESPECTIVELY WEAK, INTERMEDIATE AND STRONG INTERACTIONS BETWEEN THE ADSORBENT AND THE HYDROPHILIC MOITY OF THE SURFACTANT; THE C.M.C. IS INDICATED BY AN ARROW.

results obtained in pure water is mainly due to the formation of multilayers of horizontally oriented adsorbate molecules. A slight increase in the equilibrium concentration of DMP forms another layer of DMP molecules that lie flat. This causes an increase in adsorption.

In the pure water system at 30, 40 and 50°C and in the NaCl system at 40, 50 and 60°C this stage of the isotherm can be interpreted as follows: It occurs when neither type of displacement is favoured and the adsorbate molecules remain flat on the surface. Thus there is no sharp increase in DMP adsorption. An increase in adsorption may be due to the desolvation of DMP molecules.

In all the isotherms except that in water at 60°C, the change in amount adsorbed at the third stage of the isotherm is large. It is observed that at this stage the concentration of DMP in the bulk solution approaches the critical micelle concentration (c.m.c.) and there should be a tendency for the adsorbed molecules to aggregate in the bulk solution. This aggregation of DMP molecules orients them vertically to form a monolayer. The reason for the increased adsorption and reorientation of DMP molecules might be due to the increased lateral interactions among the DMP molecules at this surface coverage.

With a rise in temperature the increase in adsorption might be due to adsorbate-solvent interactions rather than adsorbate-adsorbent interactions. The above-mentioned orientation results in the desolvation of the adsorbate layer and formation of a second layer above the first. At a higher temperature these layers or clouds change to a lamelar mesophase which at still higher temperatures might be converted into an amorphous adsorbate phase containing a very little water. An increase in temperature (to $60^{o}C$) in pure water may also enhance the adsorbate - adsorbent interaction and/or the aggregation of the adsorbate molecules in the bulk solution, thereby resulting in a vertically oriented, more closely packed layer on the surface of the AC, DMP appears to show this type of behaviour in the pure aqueous system, when we get a single ill-defined plateau, which may be due to the formation of an incomplete monolayer. It is expected, on the basis of the theoretical value of the intercept of the Langmuir isotherm (Table 3.2), that the plateau will possibly be obtained at an equilibrium concentration (C_e) of 26 mmol l^{-1}, corresponding to a saturation capacity of 3.5 mmol g^{-1} (see Fig. 3.1a).

It has been observed that the presence of 0.1 M NaCl increases the total adsorption of DMP on AC. In fact the electrolyte alters the solubility, surface activity and aggregation properties of DMP, and this has a marked effect on adsorption at the solid-solution interface. Thus, an electrolyte that "salts out" a surfactant would increase the adsorption (6,7).

The heat of adsorption of DMP on AC is negative in both systems, indicating an usual exothermic process (Table 3.3 and Fig. 3.5),. since $40 > H_m > 25$ kJ mol^{-1}, the process appears to be physisorption leading to chemisorption (8,9). The $\triangle G_m$ values are negative in pure water and NaCl media and increase with increasing temperature (Fig. 3.6). The negative values of $\triangle G_m$ indicate the spontaneous nature of the process. The process is found to be more spontaneous in the pure water system than in the presence of NaCl. The increased spontaneous nature in the aqueous system can be explained as follows: The presence of NaCl enhanced the desolvation of $-CO_2H$ and -OH groups present on the surface of the adsorbent. Also, it decreases the hydrogen bonding between the adsorbate and adsorbent, making it less spontaneous. Further, there may be competition for adsorption between the electrolyte and DMP, thus causing a decrease in the rate of adsorption of the latter.

TABLE 3.3

Thermodynamic parameters for the adsorption of 2,6-lutidine on activated carbon at a surface coverage of 2.6 mmol g^{-1}

T (^{o}C)	Pure aqueous medium[a]			0.1 M NaCl medium[b]		
	ln C_e	ΔG_m (kJ mol^{-1})	ΔS_m (kJ $mol^{-1}K^{-1}$)	ln C_e	ΔG_m (kJ mol^{-1})	ΔS_m (kJ $mol^{-1}K^{-1}$)
30	2.8950	-7.2929	-0.0801	2.7200	-6.8510	-0.0834
40	2.5600	-6.6618	-0.0795	2.2650	-5.8942	-0.0838
50	2.1400	-5.7468	-0.0799	1.9050	-5.1157	-0.0836
60	1.7800	-4.9280	-0.0800	1.5600	-4.3190	-0.0835

[a] ΔH_m^{ads} = -31.0380 kJ mol^{-1}

[b] ΔH_m^{ads} = -32.7010 kJ mol^{-1}

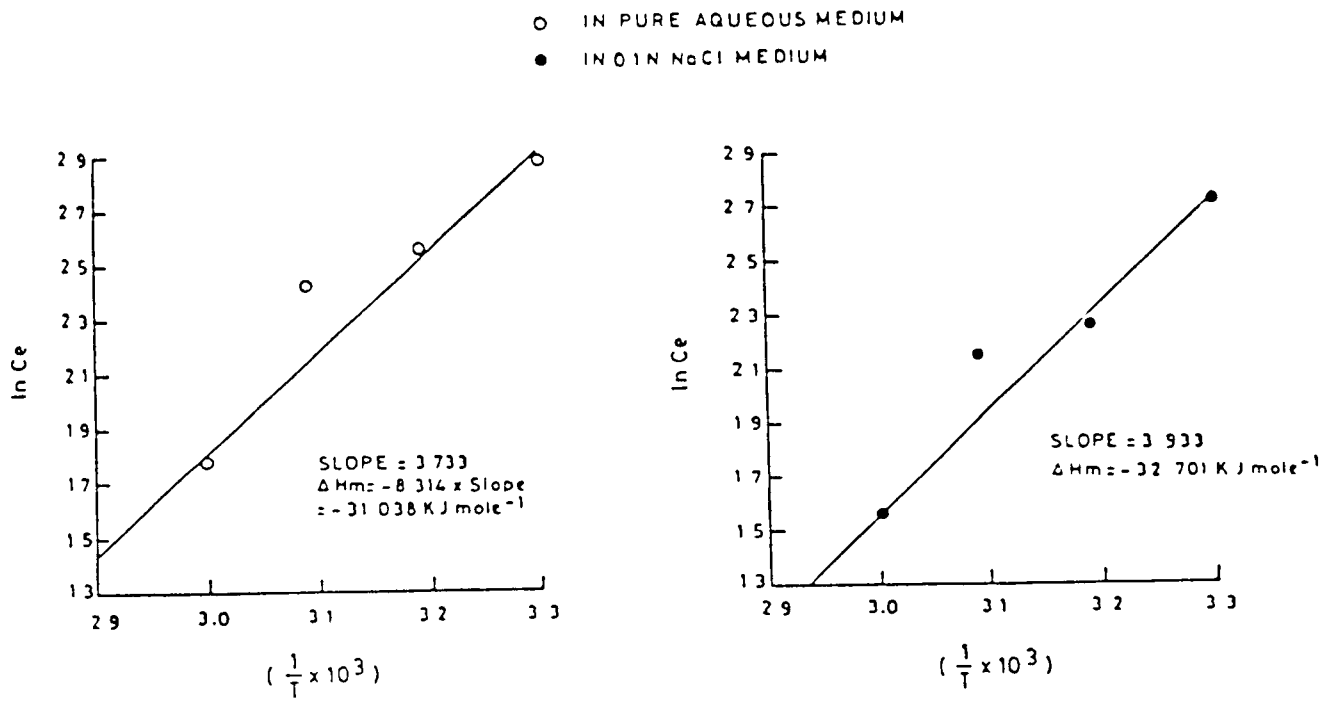

Fig. 3.5 : DETERMINATION OF ISOSTERIC ENTHALPY OF ADSORPTION AT THE SURFACE COVERAGE OF 2 6 m mole g^{-1}

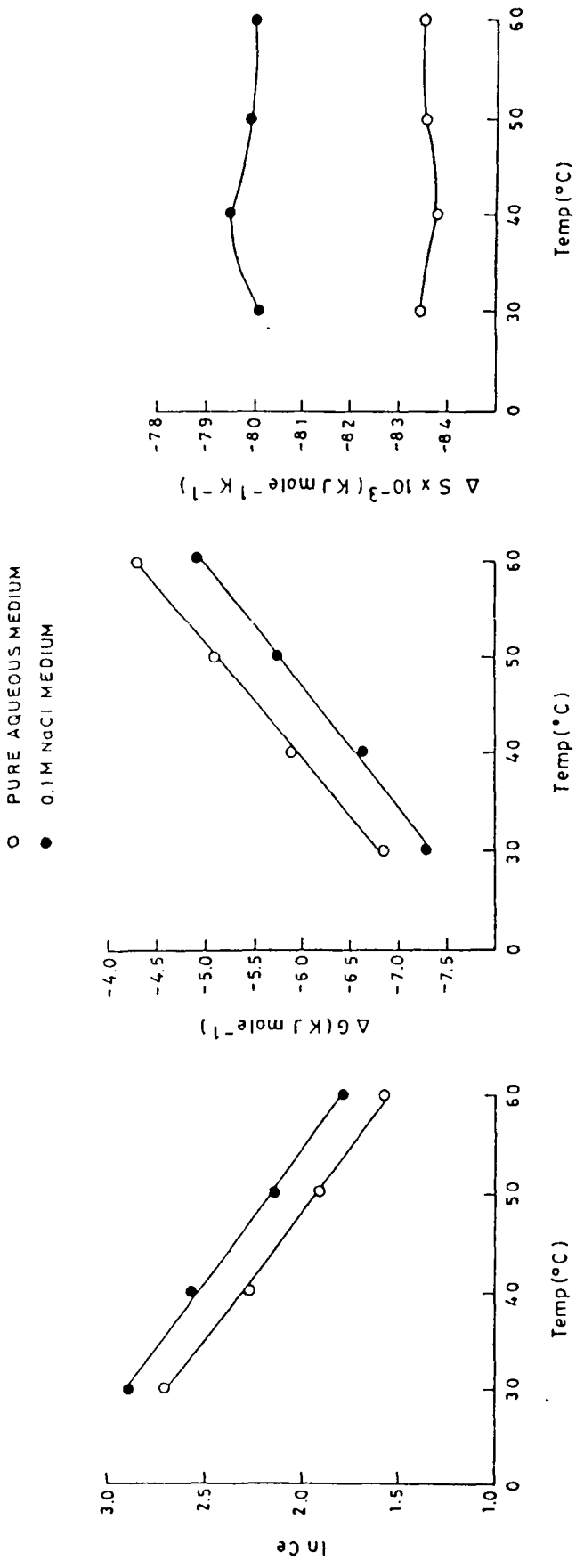

Fig. 3.6: THE PLOTS OF THERMODYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES.

As the result show, the entropy of each system remains almost constant with the rise in temperature. However, in the NaCl medium the entropy changes are more negative in comparison with pure water. This suggests an enhancement of the stability of the system, in tne presence of NaCl, perhaps due to the "salting out" effect of NaCl, as described earlier (9). This means that adsorption takes place according to the process as discussed above in the light of the free energy change. Almost constant values of the entropy data, for both systems, further support our model of adsorption of DMP lying parallel to the the surface in the L-4 type isotherm (10). On the other hand, in the L-2 type adsorption isotherm a monolayer is formed leading to the maximum adsorption of perpendicularly oriented molecules. This means that the entropy should increase in this case, whereas it remains constant, perhaps because of the increased lateral forces, which are stabilizing the perpendicularly oriented DMP molecules to the same extent as the parallel oriented molecules.

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CHAPTER - IV

EQUILIBRIUM STUDIES FOR THE FORWARD AND BACKWARD METAL-H(I) EXCHANGES ON ANTIMONY (V) ARSENOPHOSPHATE

INTRODUCTION

It has already been emphasized in Chapter-II, that water pollution is an important problem of the day. Efforts are being made now-a-days to cope with this problem by devising methods for its control and monitoring, ion exchange being one of the most promising of them (1,2). It has a great scope in the water pollution studies.

Inorganic ion exchange materials are of great importance because of their high stability under strong radiations and elevated temperatures. They have, therefore, an advantage over the organic resins which are, of course, more stable mechanically. Further, the inorganic materials illustrate a preferential selectivity for certain metal ions (3-7). This property of these materials can be advantageously explored to separate the toxic heavy metals from water in preference to the others whose presence in water can be tolerated to certain limits. Thus, these materials have a promising future in tackling the pollution problem.

In order to understand the mechanism of the preferential selectivity for certain metal ions on the surface of inorganic ion exchangers it is necessary to perform the equilibrium studies. Such a fundamental study is helpful in elucidating the ion exchange potential of these materials

under various conditions of use and is the backbone for developing the experimental knowhow for a possible commercial use of these substances. Although, the crystalline inorganic ion exchangers have received much attention in the study of their thermodynamic aspects, amorphous materials are found neglected. The possible reason may be their ill defined structures. However, since most of the materials prepared so far showing a promising analytical potential are amorphous in nature (8), their systematic thermodynamic study should be of great importance.

Earlier equilibrium studies have been performed on the materials such as amorphous and crystalline zirconium phosphate (9-16), crystalline titanium phosphate (17), amorphous cerium phosphate (18), titanium and vanadium oxides (19), tin oxide (20), manganese and nickel tungstates (21), zirconium arsenate (22), tantalum arsenate (23), iron antimonate (24), crystalline antimonic acid (25,26), crystalline antimony silicate (27), zirconium phosphosilicate (28), antimony phosphate (29,30) and antimony arsenophosphate (31). However, most of these studies have concentrated on the alkali and alkaline earth metal ions and that too for the Metal-H(I) exchanges i.e. the exchanger taken in H(I) form and subjected to the ion exchange with a metal ion.

The present studies relate mainly to the heavy metal ions generally encountered in the pollution studies such as Fe(III), Cu(II), Mn(II), Ni(II) and Hg(II). The ion exchange matrix selected for such a study has been the antimony (V) arsenophosphate and both the forward and backward exchange processes have been taken up. Antimony (V) arsenophosphate has been of considerable interest since it behaves as a cation exchanger with an excellent selectivity for these heavy metal ions (7). The following pages summarize the results of such a study. The appropriate thermodynamic parameters have been calculated and a mechanism of ion-exchange has also been proposed on the basis of these parameters.

EXPERIMENTAL

Reagents and Chemicals:

Antimony(V) chloride used in this study was a 98% purity product of Fluka, Switzerland. Trisodium orthophosphate, disodium arsenate and other reagents used were of AnalaR grade.

Apparatus:

A waterbath incubator shaker having a temperature variation of $\pm 0.5^{\circ}C$ was used for the equilibrium studies.

Synthesis of antimony(V) arsenophosphate (SbAsP):

Antimony(V) arsenophosphate was prepared by mixing the solutions of antimony(V) chloride (0.05 M) in 4 M HCl, trisodium orthophosphate (0.05 M) and disodium arsenate (0.05 M) in DMW in the volume ratio of 3:1:1. The pH of the resulting gel was fixed in the range 0-1 by adding ammonium hydroxide with constant stirring. After keeping the gel for 24 hours at room temperature, it was filtered, washed with DMW and dried in an air oven at $45^{\circ}C$.

The product thus obtained was cracked in DMW to form small granules. It was treated with 1 M HNO_3 for 24 hours,

with occasional shaking and replacing the acid, to convert into H^+ form. The material thus obtained was finally washed to pH 6-7 and dried at 45°C before sieving to uniform size (60-100 mesh). The Na^+-ion exchange capacity obtained by the column process was found to be 2.2 meq gm^{-1}.

Equilibrium Experiments:

(a) Forward Process:

Two hundred milligrams of the exchanger in H(I) form was shaken for 3 hrs in various conical flasks at 30 and 50°C with a 20 ml solution of the concerned metal ion keeping a constant ionic strength of 0.03 adjusted by adding an appropriate amount of HNO_3.

(b) Backward Process:

In the backward equilibrium experiments the exchanger (200 mg) was taken in the metal form and was shaken for 4 hours at 30 and 50°C with a 20 ml solution of HNO_3 of a constant ionic strength (0.03) adjusted by adding an appropriate amount of metal solution. The metal ions were determined volumetrically using a standard EDTA solution as a titrant. Hydrogen ions were determined by titrating against a standard NaOH solution.

Evaluation of the thermodynamic parameters:

The ion exchange process occuring on the exchanger can be represented by the equation:

$$\bar{n}H^+ + M^{n+} \rightleftharpoons \bar{M}^{n+} + nH^+ \quad \ldots\ldots\ldots (1)$$

Where M^{n+} represents the metal ion, n its valency and bar represents the ion in the exchanger phase. The equilibrium between the ionic concentration in the exchanger and solution phases is expressed as:

$$\bar{C}_H + C_M \rightleftharpoons \bar{C}_M + C_H \quad \ldots\ldots\ldots (2)$$

The equivalent ionic fractions of the metal and hydrogen ions in the two phases are calculated from the expressions:

$$\bar{X}_M = \frac{\bar{C}_M}{\bar{C}}, \quad X_M = \frac{C_M}{C}, \quad \bar{X}_H = \frac{\bar{C}_H}{\bar{C}}, \quad X_H = \frac{C_H}{C}$$

where $\bar{C}$ and C are the total electrolyte concentrations in the exchanger and solution phases respectively.

To examine the affinity for the interacting ions, the separation factors (α) and selectivity coefficients (K_c) for the Metal-H(I) and H(I)-Metal exchanges were calculated from the following expressions, assuming the ratio of the activity coefficients in the solution as unity (32,33). Under these conditions K_c ceases to express

interactions in the solution.

$$\alpha_H^M = \frac{\bar{X}_M \cdot X_H}{\bar{X}_H \cdot X_M} \qquad \ldots\ldots\ldots (3)$$

$$K_c^F = \frac{\bar{X}_M \cdot (X_H)^n}{(\bar{X}_H)^n \cdot X_M} \qquad \ldots\ldots\ldots (4)$$

for the Metal-H(I) exchange, and,

$$\alpha_M^H = \frac{\bar{X}_H \cdot X_M}{\bar{X}_M \cdot X_H} \qquad \ldots\ldots\ldots (5)$$

$$K_c^B = \frac{(X_M)^n \cdot (\bar{X}_H)}{X_H \cdot (\bar{X}_M)^n} \qquad \ldots\ldots\ldots (6)$$

for the H(I) - Metal exchange.

The thermodynamic equilibrium constants were obtained (34) from the relationship:

$$\ln K = (Z_A \backsim Z_B) + \int \ln K_c \, d\bar{X}_M \qquad \ldots\ldots\ldots (7)$$

where Z_A and Z_B are the valencies of the competing ions. The integrals were obtained from the areas under the curve obtained by plotting log K_c vs $\bar{X}_M$ using the trapezoid rule (35).

Having known the value of ln K, the standard free

energy of exchange ($\triangle G^{o}$) for the interaction (Eqn. 1) was calculated (36) from the relationship:

$$\triangle G = - RT \ln K \qquad \ldots\ldots\ldots (7)$$

where R is the universal gas constant and T is the temperature in Kelvin.

The standard enthalpy and entropy changes ($\triangle H^{o}$, and $\triangle S^{o}$) were calculated by the following equations:

$$\ln \frac{K_{T_2}}{K_{T_1}} = - \frac{\triangle H^{o}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \qquad \ldots\ldots\ldots (8)$$

and,

$$\triangle G^{o} = \triangle H^{o} - T \triangle S^{o} \qquad \ldots\ldots\ldots (9)$$

RESULTS AND DISCUSSION

Figures 4.1 and 4.2 show the results of the equilibrium versus time experiments done in both the forward and backward directions. For the forward exchange the material was taken in H(I) form while for the backward one it was taken in the metal ion form. As these figures indicate an equilibrium is attained within three hours in the forward direction and nearly four hours in the backward direction. Four hours were therefore, chosen in all the studies in order to ascertain that the equilibrium was attained.

Various values for the Metal-H(I) and H(I)-Metal exchanges, obtained at 30 and 50°C are summarized in Tables 4.1 to 4.5 and the exchange isotherms are shown in Figs. 4.3 and 4.4. As it is clear from these figures, Fe(III) ions are preferably adsorbed by antimony(V) arsenophosphate (SbAsP) phase, the preference being higher at 50°C. This conclusion is retained by the value of separation factors and selectivity coefficients (Tables 4.1 - 4.5).

Figure 4.3 shows the exchange isotherms for the exchange of Metal-H(I) systems. At 30°C, the decreasing order of uptake of the metal ions and the corresponding physical constant as well as standard and observed thermo-

TABLE 4.1

Values of separation factors and selectivity coefficients of Ni(II)-H(I) at 30 and 50°C for forward and backward exchanges on antimony(V) arsenophosphate

Sl. No.	For Foward Exchanges				For Backward Exchanges			
	α_H^{Ni}		log K_c		α_{Ni}^{H}		log K_c	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	6.273	12.270	0.795	1.098	0.235	0.402	-0.657	-0.412
2.	0.646	1.076	-0.198	0.034	0.123	0.146	-0.904	-0.908
3.	1.068	1.743	0.031	0.025	0.094	0.256	-1.169	-0.687
4.	1.118	1.118	0.053	0.053	0.216	0.373	-0.811	-0.523
5.	0.423	0.633	-0.430	-0.229	0.317	0.418	-0.638	-0.485
6.	0.309	0.557	-0.611	-0.297	0.387	0.409	-0.557	-0.437
7.	0.250	0.312	-0.747	-0.624	0.284	0.325	-0.789	-0.706
8.	0.132	0.242	-1.162	-0.790	0.187	0.247	-1.123	-0.935
9.	0.067	0.191	-1.641	-0.959	0.138	0.206	-1.394	-1.106
10.	0.007	0.086	-3.700	-2.596	0.108	0.181	-1.615	-1.228

TABLE 4.2

Values of separation factors and selectivity coefficients of Mn(II)-H(I) at 30 and 50°C for forward and backward exchanges on antimony(V) arsenophosphate

Sl. No.	For Forward Exchanges				For Backward Exchanges			
	α_H^{Mn}		log K_c		α_{Mn}^{H}		log K_c	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	11.747	0.418	1.079	-0.389	0.385	0.701	-0.437	-0.163
2.	1.051	0.604	0.022	-0.230	0.314	0.426	-0.558	-0.411
3.	0.721	1.585	-0.1525	0.211	0.213	0.261	-0.786	-0.682
4.	0.497	1.507	-0.336	0.192	0.157	0.214	-0.986	-0.832
5.	0.336	0.689	-0.547	-0.182	0.145	0.226	-1.102	-0.847
6.	0.194	0.754	0.865	0.141	0.130	0.205	-1.297	-0.949
7.	0.174	0.505	-0.953	0.356	0.149	0.215	-1.202	-0.965
8.	0.095	0.290	-1.358	-0.677	0.177	0.231	-1.135	-0.955
9.	0.034	0.139	-2.125	-1.150	0.185	0.216	-1.154	-1.038
10.	0.016	0.058	-2.784	-1.789	0.111	0.162	-1.593	-1.285

TABLE 4.3

Values of separation factors and selectivity coefficients of Hg(II)-H(I) at 30 and 50°C for forward and backward exchanges on antimony(V) arsenophosphate

Sl. No.	For Forward Exchanges				For Backward Exchanges			
	α_H^{Hg}		log K_c		α_{Hg}^{H}		log K_c	
	30°C	50°C	30°C	50°C	30°	50°C	30°C	50°C
1.	0.086	0.144	-1.108	-0.880	0.385	0.537	-0.437	-0.284
2.	0.018	0.235	-1.765	-0.673	0.287	0.436	-0.603	-0.399
3.	0.115	0.246	-1.043	-0.668	0.203	0.316	-0.799	-0.579
4.	0.128	0.257	-1.016	-0.655	0.132	0.254	-1.061	-0.699
5.	0.170	0.225	-0.888	-0.739	0.128	0.260	-1.148	-0.838
6.	0.086	0.168	-1.360	-0.916	0.138	0.210	-1.147	-0.902
7.	0.040	0.054	-1.878	-1.669	0.144	0.187	-1.173	-1.002
8.	0.031	0.041	-2.126	-1.974	0.131	0.208	-1.285	-0.980
9.	0.022	0.031	-2.398	-2.141	0.114	0.162	-1.423	-1.198
10.	0.017	0.022	-2.628	-2.420	0.092	0.124	-1.635	-1.418

TABLE 4.4

Values of separation factors and selectivity coefficients of Fe(II)-H(I) at 30 and 50°C for forward and backward exchanges on antimony(V) arsenophosphate

Sl. No.	For Forward Exchanges				For Backward exchanges			
	α_H^{Fe}		log K_c		α_{Fe}^{H}		log K_c	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	1.931	2.316	0.302	0.387	0.925	1.017	-0.035	0.008
2.	0.806	0.819	-0.101	-0.096	0.443	0.471	-0.385	-0.366
3.	0.627	0.451	-0.228	-0.400	0.279	0.379	-0.636	-0.492
4.	0.356	0.268	-0.530	-0.688	0.194	0.260	-0.856	-0.713
5.	0.270	0.193	-0.674	-0.897	0.172	0.218	-0.960	-0.830
6.	0.203	0.146	-0.850	-1.090	0.163	0.164	-1.057	-1.047
7.	0.181	0.175	-0.942	-1.011	0.156	0.157	-1.127	-1.127
8.	0.135	0.171	-1.148	-1.039	0.132	0.159	-1.272	-1.172
9.	0.130	0.139	-1.229	-1.193	0.098	0.141	-1.07	-1.295
10.	0.109	0.135	-1.378	-1.297	0.044	0.061	-2.242	-1.990

TABLE 4.5

Values of separation factors and selectivity coefficients of Cu(II)-H(I) at 30 and 50°C for forward and backward exchanges on antimony(V) arsenophosphate

Sl. No.	For Forward Exchanges				For Backward Exchanges			
	α_H^{Cu}		log K_c		α_{Cu}^{H}		log K_c	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
1.	1.051	1.000	0.022	0.000	1.000	2.031	0.000	0.314
2.	1.000	0.975	0.000	-0.011	0.802	1.863	-0.120	0.282
3.	1.000	1.017	0.000	0.007	1.256	1.652	0.104	0.218
4.	1.013	1.013	0.006	0.006	0.572	0.74	-0.271	-0.145
5.	0.376	0.534	-0.103	-0.307	0.376	0.465	-0.498	-0.384
6.	0.202	0.363	-0.833	-0.517	0.240	0.305	-0.766	-0.634
7.	0.081	0.166	-1.416	-0.933	0.202	0.323	-0.888	-0.659
8.	0.058	0.098	-1.667	-1.323	0.168	0.220	-1.019	-0.869
9.	0.041	0.031	-1.938	-2.175	0.134	0.178	-1.195	-1.044
10.	0.003	0.013	-3.961	-2.850	0.113	0.128	-1.340	-1.283

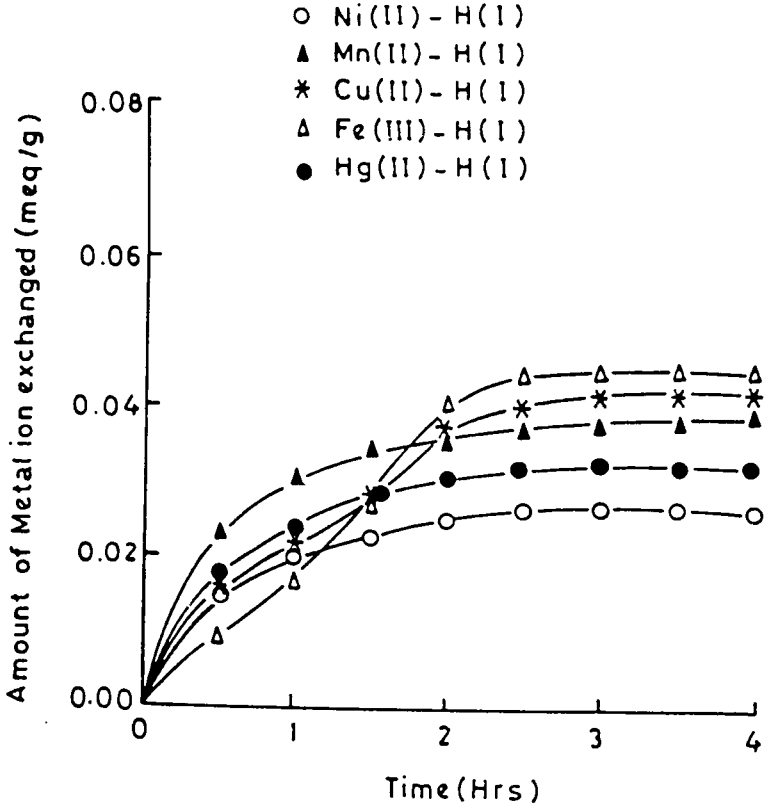

Fig. 4.1: Plots of the amount exchanged of Mn(II), Fe(III), Cu(II), Ni(II) and Hg(II) with H(I) versus time on Antimony (V) arsenophosphate.

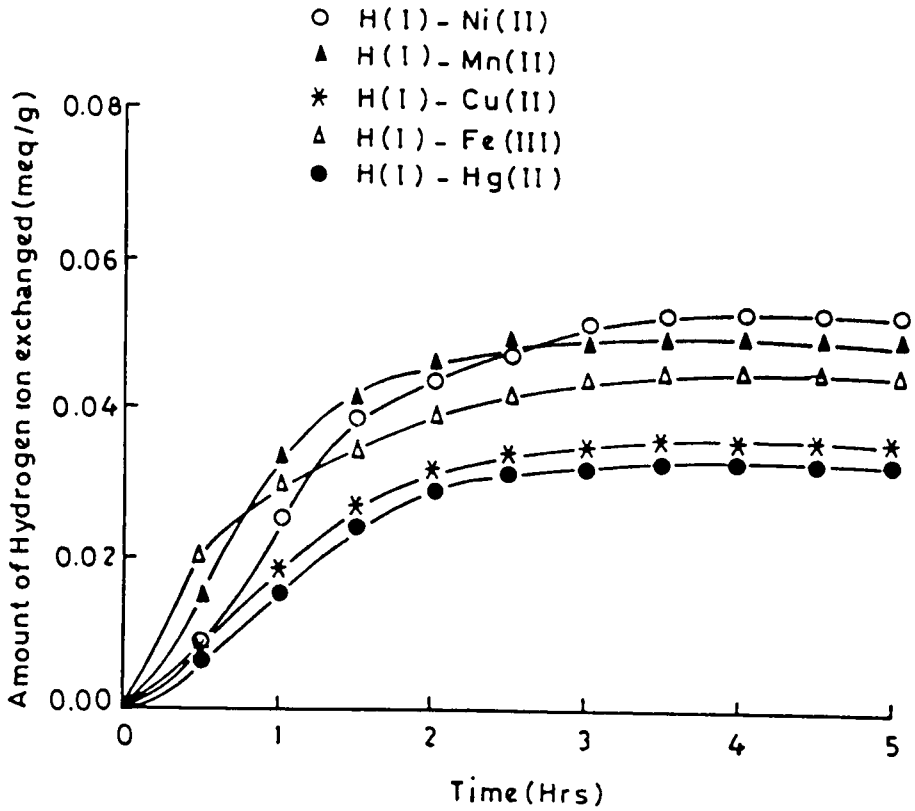

Fig. 4.2: Plots of amount exchanged of H(I) with Mn(II), Fe(III), Cu(II), Ni(II) and Hg(II) versus time on Antimony (V) arsenophosphate.

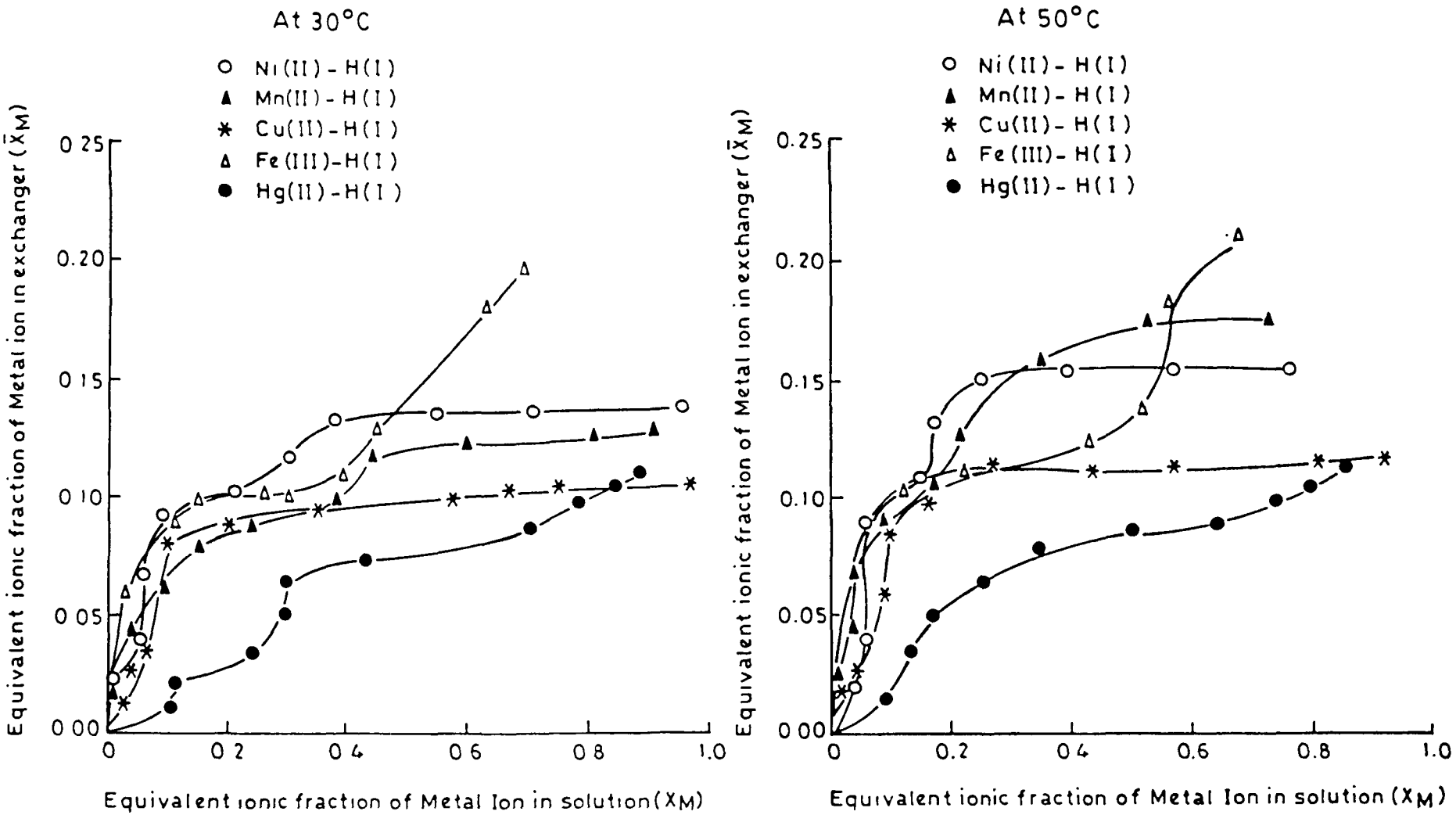

Fig. 4.3: Exchange isotherms of the Mn(II) - H(I), Ni(II) - H(I), Fe(III) - H(I), Cu(II) - H(I) and Hg(II) - H(I) exchanges on Antimony (V) arsenophosphate at 30° and 50°C.

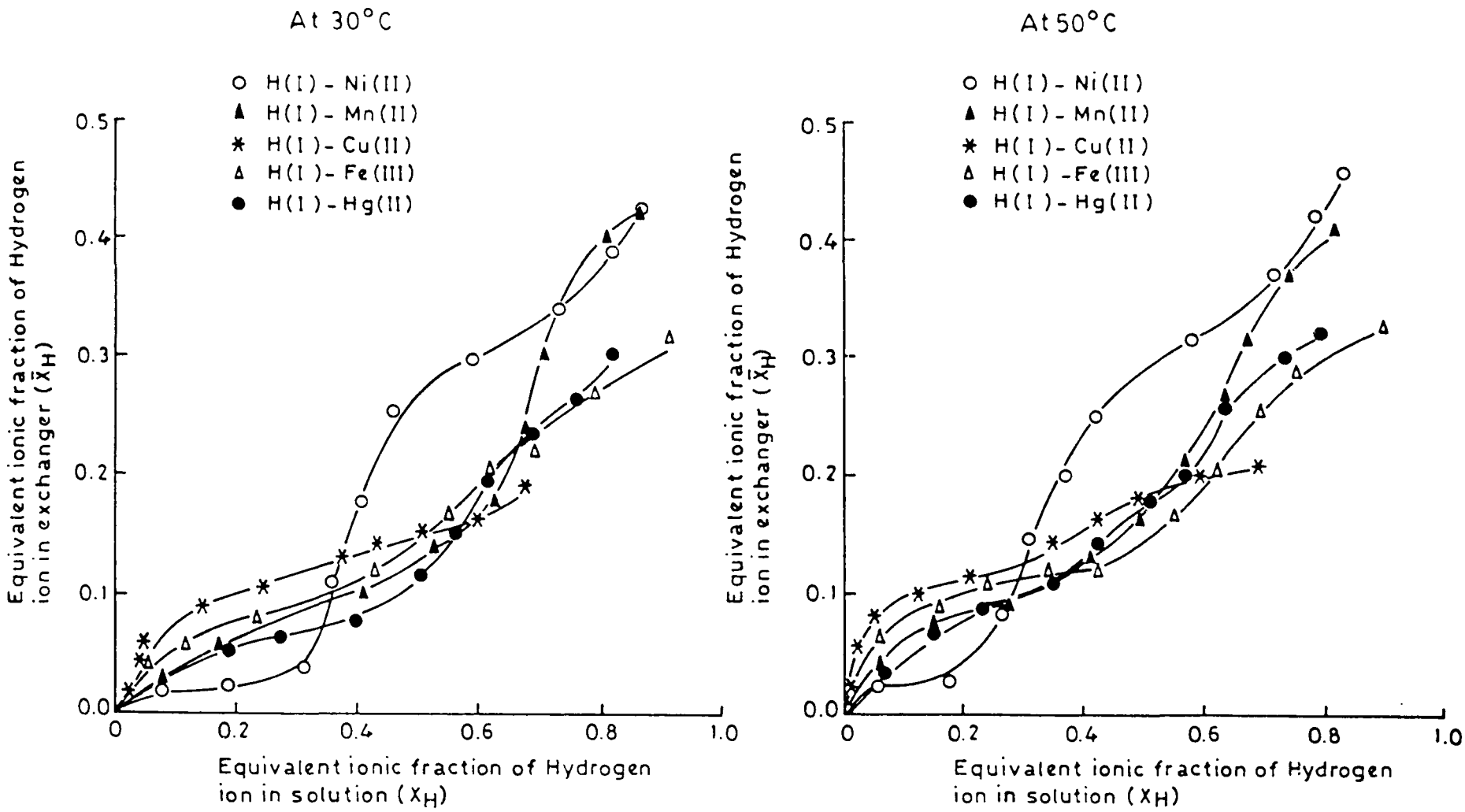

Fig. 4.4: Exchange isotherms of the H(I)-Mn(II), H(I)-Ni(II), H(I)-Fe(III), H(I)-Cu(II) and H(I)-Hg(II) exchanges on Antimony (V) arseno phosphate at 30° and 50°C.

dynamic parameters (37) are given in Tables 4.6 and 4.8. The overall order of uptake is Fe(III) > Ni(II) > Mn(II) > Cu(II) > Hg(II). The theoretical examination of the data reveals that this process is highly influenced by the chemical and physical nature of the metal ions. On the basis of the chemical nature the above series can be devided into following sub groups viz. (a) Fe(III) > Ni(II) > Mn(II) and (b) Cu(II) > Hg(II). In each of these groups the extent of exchange of the metal ions is parallel to the hydrated ionic radii. Further, the entropy of the process also increases with the increase in exchange. This suggests that the exchange of all these metal ions occurs in unhydrated forms. The metal ions, probably, shed some part of their hydration shell at the surface of the exchanger upto the extent their sizes are fit for the migration through the pores of cavity. They migrate upto the exchange sites in unhydrated forms and then get hydrated after being exchanged causing thereby the distortion of the matrix. Further, this distortion is parallel to their hydrated ionic radii. Hence, the entropy of the systems increases with the increase in hydrated ionic sizes of these metal ions.

The overall process is endothermic and spontaneous as indicated by the enthalpy and free energy data respectively.

TABLE 4.6

Thermodynamic values of Ni(II)-H(I), Mn(II)-H(I), Hg(II)-H(I), Fe(III)-H(I) and Cu(II)-H(I) exchanges at 30 and 50°C on antimony(V) arsenophosphate cation exchanger

Thermodynamic parameter	Values for the Ni(II)-H(I) system at		Values for the Mn(II)-H(I) system at		Values for the Hg(II)-H(I) system at		Values for the Fe(III)-H(I) system at		Values for the Cu(II)-H(I) system at	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
K	37.62	52.47	22.98	27.23	15.56	16.38	23.38	32.87	25.06	27.58
$\triangle G^{o}$ (KJ mol^{-1})	- 9.14	-10.65	-7.89	-8.87	-6.93	-7.51	-7.94	-9.38	-8.12	-8.91
$\triangle H^{o}$ (KJ mol^{-1})	5.86		6.88		2.08		13.82		3.88	
$\triangle S^{o}$ (K $mol^{-1}K^{-1}$)	49.51	51.14	48.74	48.76	29.70	29.69	71.81	71.83	39.60	39.59

TABLE 4.7

Thermodynamic values of H(I)-Ni(II), H(I)-Mn(II), H(I)-Hg(II), H(I)-Fe(III) and H(I)-Cu(II) exchanges at 30 and 50°C on antimony(V) arsenophosphate cation exchanger

Thermodynamic parameter	Values for the H(I)-Ni(II) system at		Values for the H(I)-Mn(II) system at		Values for the H(I)-Hg(II) system at		Values for the H(I)-Fe(III) system at		Values for the H(I)-Cu(II) system at	
	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C	30°C	50°C
K	0.99	1.68	0.26	0.36	0.25	0.26	0.46	0.61	0.23	0.24
$\triangle G^{\circ}$ (KJ mol^{-1})	0.25	-1.39	3.39	2.74	3.49	3.62	1.93	1.34	3.70	3.60
$\triangle H^{\circ}$ (KJ mol^{-1})	9.32		13.19		1.59		11.45		1.73	
$\triangle S^{\circ}$ (J $mol^{-1}K^{-1}$)	29.90	33.00	32.36	32.37	6.30	6.20	31.40	31.20	6.52	5.85

TABLE 4.8

Absolute Thermodynamic data for aqueous ions at 25°C (Ref. 37)

Ion	Ionic radii (°A)	Hydrated ionic radii (°A)	ΔH^{o}_{Hyd} (kJ mol^{-1})	ΔS^{o}_{Hyd} (J $mol^{-1}K^{-1}$)	ΔG^{o}_{Hyd} (kJ mol^{-1})
H(I)	2.08	9.0	-1121	-123	-1084
Cu(II)	0.69	6.0	-2161	302	-2071
Ni(II)	0.72	6.0	-2174	-369	-2056
Fe(III)	0.64	9.0	-4343	-506	-4192
Mn(II)	0.80	6.0	-1905	-286	-1820
Hg(II)	1.10	5.0	-	-	-

The spontaniety of the process increases with the decrease in their ionic size. This further supports the model proposed above. The only anomaly in the system is shown by Ni(II) which can be explained in terms of Jahn Teller effect. In aqueous solution Ni(II) has an octahedral primary solvation shell while Cu(II) has a tetragonally distorted primary solvation shell as a consequence of the said effect. If the exchanging ions could have maintained the similar configuration as were in aqueous solution, a large steric effect would have been operative for Ni(II) and decreased steric effect, due to larger Jahn Teller deformation, for $Cu(H_2O)_6^{2+}$ (26). Since these metal ions exchange on antimony(V) arsenophosphate in unhydrated form, the said configuration of the aqueous solution is no longer maintained and reverse effect is observed i.e. Ni(II) shows less steric hindrance than Cu(II) during the migration into the exchanger phase. Thus the exchange of Ni(II) is the most spontaneous process in the systems studied.

The equilibrium concentration plays an important role in the extent of uptake. It is evident from the Figure 4.3, that at a lower concentration, the order of uptake of these metal ions is different i.e. Ni(II) > Fe(III)> Cu(II) > Mn(II) > Hg(II). This order is exactly reverse

to that observed for antimonic acid (26) probably because of the reverse type of mechanism explained above.

Effect of increase in temperature becomes clear on comparing the isotherms at 30 and 50°C (Figure 4.3). The overall order of exchange of these metal ions becomes Fe(III)> Mn(II) >Ni(II) >Cu(II) >Hg(II). This series is not exactly parallel to the ionic radii and anomalous behaviour is shown by Mn(II) which is exchanged to a greater extent than Ni(II). The anomalous behaviour of Mn(II) was also observed in case of antimonic acid (26). It is interesting to note that the trend of thermodynamic parameters is similar to that observed at 30°C and only the total uptake of Mn(II) is increased. This phenomenon may be explained in terms of unique behaviour of Mn(II) (d_5 system) among all bivalent transition metal ions. Free energy change is negative for all the forward processes means that metal ions are preferably adsorbed on SbAsP surface as compared to H(I) ions.

The thermodynamic equilibrium constant (K) is highest for Ni(II) ion in the forward exchange followed by Cu(II), Fe(III), Mn(II) and Hg(II), indicating the affinities for different metal ions in that order. At 50°C, however, the K values are in the order Ni(II)> Fe(III) > Cu(II) >Mn(II) >Hg(II). The exchanger shows

greater affinity for Ni(II) ion at both the temperatures and the orders are the same except for Fe(III), Cu(II) and Mn(II).

Free energy change is negative for all the forward processes which means that metal ions are adsorbed preferably to the H(I)/ions on SbAsP surface, and the preference increases with the rise in temperature. However in the backward direction it is negative only for the H(I)-Ni(II) exchange, indicating an easier elution of Ni(II) with an acid.

The standard enthalpy and entropy changes are positive for both the forward and backward processes. A positive enthalpy change indicates that these exchanges are endothermic. Positive values of standard entropy change suggest that the metal ions are less strongly bound to the exchanger than H(I) ions.

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CHAPTER - V

EVALUATION OF THE DIMENSIONLESS TIME PARAMETER FOR SOME PARTICLE DIFFUSION CONTROLLED FORWARD AND REVERSE H(I)-CATION(I), OH(I)-ANION(I) AND OH(I) - ANION(I)) EXCHANGES

INTRODUCTION

Inorganic ion exchangers are well established materials for the separation of metal ions (1-13). The rate factor in the ion exchange process is of great importance for the economic and industrial employment of these materials. In true ion exchange and for a particle diffusion controlled phenomenon where the fluxes of at least two different ionic species are coupled with one another (14), the non linear Nernst - Planck equations are applicable with some additional assumptions (15,16). For this a knowledge of dimensionless time parameter (Υ) is important because it makes the calculations much easier for the evaluation of kinetic parameters. This dimensionless time parameter (Υ) involves the diffusion coefficient of the counter ion which is initially in the ion exchanger, i.e. $\bar{D}_A$ in one case and $\bar{D}_B$ in the other. When the same time scale is used for forward and reverse exchange, it becomes apparant that the exchange is faster, when the faster counter ion is initially in the ion exchanger, and that the difference in rate increases as conversion progresses. The graphical method used earlier (17-22) taking into consideration the explicit expression of Helfferich (23,24) was tedious and gives only the approximate Υ values. To improve the accuracy of results a

programme was instituted in these laboratories (25) for evaluating this parameter τ , by the computer method. The τ values obtained, however, were only for H(I) - Metal (II) exchange systems in both the forward and reverse processes.

This chapter is an extension of such a study and deals with the results obtained for the dimensionless time parameter τ , for the particle diffusion controlled forward and reverse H(I) - Cation(I), OH(I) - Anion(I) and OH(I) - Anion(II) exchanges.

RESULTS AND DISCUSSION

The fractional attainment of equilibrium, $U_{(\tau)}$ may be expressed as:

$$U_{(\tau)} = \frac{\text{The amount of exchange at time t}}{\text{The amount of exchange at infinite time (equilibrium)}} \quad \ldots\ldots (1)$$

According to the explicit approximation given by Helfferich et al. (23,24) the fractional attainment of equilibrium for a particle diffusion controlled phenomenon is given by

$$U_{(\tau)} = \left\{1-\exp\left[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)\right]\right\}^{1/2} \quad \ldots\ldots (2)$$

where $\tau = \bar{D}_A t/r_0^2$ and mobility ratio, $\alpha = \bar{D}_A/\bar{D}_B$. The coefficients of counter ions A and B respectively in the ion exchanger phase, r_0 is the bead radius and t is the time.

For monovalent counter ions (cations or anions)

A monovalent ion exchange phenomenon may be expressed as follows:

$$\bar{R}A + B_{(Sol.)} \rightleftharpoons \bar{R}B + A_{(Sol.)}$$

(where the barred symbols denote the ion exchanger phase)

For the above process, both in the forward and reverse directions, the coefficients are given by

$f_1(\alpha) = -1/(0.57 + 0.43\alpha^{0.775})$

$f_2(\alpha) = 1/(0.26 + 0.782\alpha)$

$f_3(\alpha) = -1/(0.165 + 0.177\alpha)$

in the range $0.1 \leqslant \alpha \leqslant 10$.

<u>For bivalent anions</u>

A bivalent anion exchange equation may be given as:

$$2\bar{R}^{+}OH^{-} + A^{2-} \rightleftharpoons \bar{R}_2^{+} A^{2-} + 2OH^{-}$$

For the forward process i.e. if the ion exchanger is taken in the OH(I) form and the exchanging ion is A(II) then the coefficients are given, in the range $1 \leqslant \alpha \leqslant 20$, by

$f_1(\alpha) = -1/(0.64 + 0.36\alpha^{0.668})$

$f_2(\alpha) = -1/(0.96 - 2.0\alpha^{0.4635})$

$f_3(\alpha) = -1/(0.27 + 0.09\alpha^{1.14})$

For the reverse process i.e., when the ion exchanger is in the A(II) form and the exchanging ion is CH(I) we have

$$f_1(\alpha) = -1/(0.35 + 0.65\alpha^{0.86})$$

$$f_2(\alpha) = 1/(0.03 + 1.012\alpha^{2.06})$$

$$f_3(\alpha) = -1/(0.00265 + 0.354\alpha^{2.671})$$

in the range $0.05 \leqslant \alpha \leqslant 1$ and $0 \leqslant \tau \leqslant 0.04$ and

$$f_1(\alpha) = -1/(0.438 + 0.562\alpha^{0.777})$$

$$f_2(\alpha) = 1/(0.127 + 0.915\alpha^{1.057})$$

$$f_3(\alpha) = 1/(0.008 - 0.365\alpha^{0.453})$$

for $0.05 \leqslant \alpha \leqslant 1$ and $\tau \geqslant 0.04$.

The τ values obtained from Equation-2 for the forward and reverse exchange of H(I) with some monovalent cations, OH(I) with some monovalent and bivalent anions are given in Tables 5.1-5.6 for the various fractional exchange values. A computer, model VAX 11/780 manufactured by the digital equipment corporation, Maynard, MA, was used for these calculations.

TABLE 5.1

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled H(I)-Cation(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium U_τ	Dimensionless time, τ			
	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Rb}}$ = 4.494	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Cs}}$ = 4.529	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Tl}}$ = 4.681	$\alpha = \frac{\bar{D}_H}{\bar{D}_{NH_4}}$ = 4.751
0.01	1.974×10^{-5}	1.983×10^{-5}	2.019×10^{-5}	2.037×10^{-5}
0.05	4.942×10^{-4}	4.963×10^{-4}	5.054×10^{-4}	5.099×10^{-4}
0.10	1.986×10^{-3}	1.994×10^{-3}	2.031×10^{-3}	2.049×10^{-3}
0.15	4.502×10^{-3}	4.521×10^{-3}	4.604×10^{-3}	4.646×10^{-3}
0.20	8.090×10^{-3}	8.125×10^{-3}	8.274×10^{-3}	8.348×10^{-3}
0.25	1.282×10^{-2}	1.287×10^{-2}	1.311×10^{-2}	1.323×10^{-2}
0.30	1.878×10^{-2}	1.886×10^{-2}	1.921×10^{-2}	1.938×10^{-2}
0.35	2.611×10^{-2}	2.622×10^{-2}	2.670×10^{-2}	2.694×10^{-2}
0.40	3.496×10^{-2}	3.511×10^{-2}	3.575×10^{-2}	3.607×10^{-2}
0.45	4.554×10^{-2}	4.573×10^{-2}	4.658×10^{-2}	4.699×10^{-2}
0.50	5.813×10^{-2}	5.838×10^{-2}	5.945×10^{-2}	5.998×10^{-2}
0.55	7.307×10^{-2}	7.338×10^{-2}	7.472×10^{-2}	7.539×10^{-2}
0.60	9.082×10^{-2}	9.121×10^{-2}	9.286×10^{-2}	9.369×10^{-2}
0.65	1.120×10^{-1}	1.125×10^{-1}	1.145×10^{-1}	1.155×10^{-1}
0.70	1.374×10^{-1}	1.379×10^{-1}	1.404×10^{-1}	1.416×10^{-1}
0.75	1.681×10^{-1}	1.688×10^{-1}	1.717×10^{-1}	1.731×10^{-1}
0.80	2.058×10^{-1}	2.066×10^{-1}	2.101×10^{-1}	2.118×10^{-1}
0.85	2.532×10^{-1}	2.541×10^{-1}	2.581×10^{-1}	2.601×10^{-1}
0.90	3.155×10^{-1}	3.166×10^{-1}	3.212×10^{-1}	3.235×10^{-1}
0.95	4.078×10^{-1}	4.090×10^{-1}	4.144×10^{-1}	4.171×10^{-1}
0.99	5.680×10^{-1}	5.695×10^{-1}	5.760×10^{-1}	5.793×10^{-1}

(TABLE 5.1 CONTINUED)

Fractional attainment of equilibrium $U_{(\tau)}$	Dimensionless time, τ				
	$\alpha = \frac{\bar{D}_H}{\bar{D}_K}$ = 4.758	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Ag}}$ = 5.648	$\alpha = \frac{\bar{D}_H}{\bar{D}_{N_2H_5}}$ = 5.926	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Na}}$ = 6.982	$\alpha = \frac{\bar{D}_H}{\bar{D}_{Li}}$ = 9.044
0.01	2.037×10^{-5}	2.245×10^{-5}	2.308×10^{-5}	2.543×10^{-5}	2.929×10^{-5}
0.05	5.100×10^{-4}	5.619×10^{-4}	5.778×10^{-4}	6.365×10^{-4}	7.457×10^{-4}
0.10	2.049×10^{-3}	2.258×10^{-3}	2.322×10^{-3}	2.558×10^{-3}	2.997×10^{-3}
0.15	4.646×10^{-3}	5.120×10^{-3}	5.264×10^{-3}	5.799×10^{-3}	6.796×10^{-3}
0.20	8.349×10^{-3}	9.200×10^{-3}	9.460×10^{-3}	1.042×10^{-2}	1.221×10^{-2}
0.25	1.323×10^{-2}	1.458×10^{-2}	1.499×10^{-2}	1.652×10^{-2}	1.936×10^{-2}
0.30	1.939×10^{-2}	2.136×10^{-2}	2.197×10^{-2}	2.421×10^{-2}	2.837×10^{-2}
0.35	2.695×10^{-2}	2.970×10^{-2}	3.054×10^{-2}	3.365×10^{-2}	3.944×10^{-2}
0.40	3.608×10^{-2}	3.973×10^{-2}	4.088×10^{-2}	4.505×10^{-2}	5.280×10^{-2}
0.45	4.700×10^{-2}	5.179×10^{-2}	5.325×10^{-2}	5.867×10^{-2}	6.874×10^{-2}
0.50	5.999×10^{-2}	6.609×10^{-2}	6.794×10^{-2}	7.484×10^{-2}	8.764×10^{-2}
0.55	7.540×10^{-2}	8.303×10^{-2}	8.535×10^{-2}	9.396×10^{-2}	1.099×10^{-1}
0.60	9.370×10^{-2}	1.031×10^{-1}	1.060×10^{-1}	1.166×10^{-1}	1.361×10^{-1}
0.65	1.155×10^{-1}	1.270×10^{-1}	1.305×10^{-1}	1.433×10^{-1}	1.669×10^{-1}
0.70	1.416×10^{-1}	1.554×10^{-1}	1.596×10^{-1}	1.750×10^{-1}	2.031×10^{-1}
0.75	1.732×10^{-1}	1.896×10^{-1}	1.946×10^{-1}	2.128×10^{-1}	2.457×10^{-1}
0.80	2.118×10^{-1}	2.311×10^{-1}	2.369×10^{-1}	2.581×10^{-1}	2.962×10^{-1}
0.85	2.602×10^{-1}	2.826×10^{-1}	2.893×10^{-1}	3.137×10^{-1}	3.571×10^{-1}
0.90	3.235×10^{-1}	3.494×10^{-1}	3.571×10^{-1}	3.850×10^{-1}	4.340×10^{-1}
0.95	4.172×10^{-1}	4.471×10^{-1}	4.560×10^{-1}	4.880×10^{-1}	5.440×10^{-1}
0.99	5.793×10^{-1}	6.153×10^{-1}	6.260×10^{-1}	6.643×10^{-1}	7.309×10^{-1}

TABLE 5.2

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled Cation(I)-H(I) exchanges involving different mobility ratios.

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ			
	$\alpha = \frac{\bar{D}_{Rb}}{\bar{D}_H}$ = 0.223	$\alpha = \frac{\bar{D}_{Cs}}{\bar{D}_H}$ = 0.221	$\alpha = \frac{\bar{D}_{Tl}}{\bar{D}_H}$ = 0.214	$\alpha = \frac{\bar{D}_{NH_4/K}}{\bar{D}_H}$ = 0.210
0.01	7.139×10^{-6}	7.129×10^{-6}	7.096×10^{-6}	7.077×10^{-6}
0.05	1.787×10^{-4}	1.785×10^{-4}	1.776×10^{-4}	1.772×10^{-4}
0.10	7.181×10^{-4}	7.172×10^{-4}	7.138×10^{-4}	7.119×10^{-4}
0.15	1.628×10^{-3}	1.626×10^{-3}	1.619×10^{-3}	1.614×10^{-3}
0.20	2.927×10^{-3}	2.923×10^{-3}	2.910×10^{-3}	2.902×10^{-3}
0.25	4.641×10^{-3}	4.635×10^{-3}	4.613×10^{-3}	4.601×10^{-3}
0.30	6.805×10^{-3}	6.796×10^{-3}	6.765×10^{-3}	6.746×10^{-3}
0.35	9.469×10^{-3}	9.457×10^{-3}	9.413×10^{-3}	9.388×10^{-3}
0.40	1.270×10^{-2}	1.268×10^{-2}	1.262×10^{-2}	1.259×10^{-2}
0.45	1.658×10^{-2}	1.656×10^{-2}	1.648×10^{-2}	1.644×10^{-2}
0.50	2.123×10^{-2}	2.120×10^{-2}	2.111×10^{-2}	2.105×10^{-2}
0.55	2.681×10^{-2}	2.678×10^{-2}	2.666×10^{-2}	2.659×10^{-2}
0.60	3.355×10^{-2}	3.350×10^{-2}	3.336×10^{-2}	3.327×10^{-2}
0.65	4.176×10^{-2}	4.171×10^{-2}	4.153×10^{-2}	4.143×10^{-2}
0.70	5.195×10^{-2}	5.189×10^{-2}	5.167×10^{-2}	5.154×10^{-2}
0.75	6.489×10^{-2}	6.481×10^{-2}	6.454×10^{-2}	6.439×10^{-2}
0.80	8.190×10^{-2}	8.181×10^{-2}	8.149×10^{-2}	8.131×10^{-2}
0.85	1.055×10^{-1}	1.054×10^{-1}	1.050×10^{-1}	1.048×10^{-1}
0.90	1.411×10^{-1}	1.410×10^{-1}	1.406×10^{-1}	1.404×10^{-1}
0.95	2.045×10^{-1}	2.044×10^{-1}	2.040×10^{-1}	2.038×10^{-1}
0.99	3.322×10^{-1}	3.322×10^{-1}	3.322×10^{-1}	3.322×10^{-1}

(TABLE 5.2 CONTINUED)

Fractional attainment of equilibrium $U_{(\tau)}$	Dimensionless time, τ			
	$\alpha = \frac{\bar{D}_{Ag}}{\bar{D}_H}$ = 0.177	$\alpha = \frac{\bar{D}_{N_2H_5}}{\bar{D}_H}$ = 0.168	$\alpha = \frac{\bar{D}_{Na}}{\bar{D}_H}$ = 0.143	$\alpha = \frac{\bar{D}_{Li}}{\bar{D}_H}$ = 0.111
0.01	6.915×10^{-6}	6.870×10^{-6}	6.742×10^{-6}	6.570×10^{-6}
0.05	1.731×10^{-4}	1.720×10^{-4}	1.688×10^{-4}	1.645×10^{-4}
0.10	6.997×10^{-4}	6.912×10^{-4}	6.783×10^{-4}	6.610×10^{-4}
0.15	1.578×10^{-3}	1.567×10^{-3}	1.538×10^{-3}	1.499×10^{-3}
0.20	2.836×10^{-3}	2.813×10^{-3}	2.765×10^{-3}	2.695×10^{-3}
0.25	4.496×10^{-3}	4.467×10^{-3}	4.384×10^{-3}	4.275×10^{-3}
0.30	6.594×10^{-3}	6.551×10^{-3}	6.430×10^{-3}	6.267×10^{-3}
0.35	9.176×10^{-3}	9.117×10^{-3}	8.949×10^{-3}	8.723×10^{-3}
0.40	1.251×10^{-2}	1.223×10^{-2}	1.200×10^{-2}	1.170×10^{-2}
0.45	1.607×10^{-2}	1.597×10^{-2}	1.568×10^{-2}	1.529×10^{-2}
0.50	2.059×10^{-2}	2.046×10^{-2}	2.008×10^{-2}	1.959×10^{-2}
0.55	2.600×10^{-2}	2.584×10^{-2}	2.538×110^{-2}	2.475×10^{-2}
0.60	3.255×10^{-2}	3.235×10^{-2}	3.178×10^{-2}	3.101×10^{-2}
0.65	4.054×10^{-2}	4.030×10^{-2}	3.960×10^{-2}	3.865×10^{-2}
0.70	5.047×10^{-2}	5.017×10^{-2}	4.932×10^{-2}	4.817×10^{-2}
0.75	6.310×10^{-2}	6.274×10^{-2}	6.171×10^{-2}	6.033×10^{-2}
0.80	7.977×10^{-2}	7.934×10^{-2}	7.811×10^{-2}	7.647×10^{-2}
0.85	1.030×10^{-1}	1.025×10^{-1}	1.011×10^{-1}	9.916×10^{-2}
0.90	1.384×10^{-1}	1.379×10^{-1}	1.363×10^{-1}	1.343×10^{-1}
0.95	2.083×10^{-1}	2.018×10^{-1}	2.007×10^{-1}	1.994×10^{-1}
0.99	3.324×10^{-1}	3.326×10^{-1}	3.334×10^{-1}	3.351×10^{-1}

TABLE 5.3

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled OH(I)-A(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ						
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{IO_3}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{F}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{BrO_3}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{MnO_4}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{ClO_3/CNO/OCN}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SCN}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{ClO_4}}$
	= 4.889	= 3.574	= 3.554	= 3.230	= 3.065	= 3.000	= 2.942
0.01	2.068×10^{-5}	1.747×10^{-5}	1.742×10^{-5}	1.659×10^{-5}	1.616×10^{-5}	1.599×10^{-5}	1.583×10^{-5}
0.05	5.178×10^{-4}	4.373×10^{-4}	4.360×10^{-4}	4.152×10^{-4}	4.045×10^{-4}	4.002×10^{-4}	3.963×10^{-4}
0.10	2.081×10^{-3}	1.757×10^{-3}	1.752×10^{-3}	1.668×10^{-3}	1.625×10^{-3}	1.608×10^{-3}	1.593×10^{-3}
0.15	4.717×10^{-3}	3.984×10^{-3}	3.972×10^{-3}	3.782×10^{-3}	3.684×10^{-3}	3.645×10^{-3}	3.610×10^{-3}
0.20	8.477×10^{-3}	7.158×10^{-3}	7.138×10^{-3}	6.997×10^{-3}	6.620×10^{-3}	6.550×10^{-3}	6.687×10^{-3}
0.25	1.343×10^{-2}	1.134×10^{-2}	1.131×10^{-2}	1.077×10^{-2}	1.049×10^{-2}	1.038×10^{-2}	1.028×10^{-2}
0.30	1.968×10^{-2}	1.662×10^{-2}	1.657×10^{-2}	1.578×10^{-2}	1.537×10^{-2}	1.521×10^{-2}	1.506×10^{-2}
0.35	2.736×10^{-2}	2.310×10^{-2}	2.303×10^{-2}	2.193×10^{-2}	2.136×10^{-2}	2.114×10^{-2}	2.093×10^{-2}
0.40	3.663×10^{-2}	3.093×10^{-2}	3.084×10^{-2}	2.937×10^{-2}	2.860×10^{-2}	2.830×10^{-2}	2.803×10^{-2}
0.45	4.772×10^{-2}	4.030×10^{-2}	4.018×10^{-2}	3.826×10^{-2}	3.727×10^{-2}	3.688×10^{-2}	3.652×10^{-2}
0.50	6.092×10^{-2}	5.145×10^{-2}	5.130×10^{-2}	4.885×10^{-2}	4.759×10^{-2}	4.709×10^{-2}	4.664×10^{-2}
0.55	7.654×10^{-2}	6.470×10^{-2}	6.451×10^{-2}	6.145×10^{-2}	5.986×10^{-2}	5.923×10^{-2}	5.867×10^{-2}
0.60	9.511×10^{-2}	8.048×10^{-2}	8.025×10^{-2}	7.646×10^{-2}	7.449×10^{-2}	7.371×10^{-2}	7.301×10^{-2}
0.65	1.172×10^{-1}	9.935×10^{-2}	9.907×10^{-2}	9.443×10^{-2}	9.202×10^{-2}	9.106×10^{-2}	9.021×10^{-2}
0.70	1.437×10^{-1}	1.221×10^{-1}	1.217×10^{-1}	1.161×10^{-1}	1.132×10^{-1}	1.120×10^{-1}	1.110×10^{-1}
0.75	1.756×10^{-1}	1.498×10^{-1}	1.494×10^{-1}	1.426×10^{-1}	1.391×10^{-1}	1.377×10^{-1}	1.364×10^{-1}
0.80	2.147×10^{-1}	1.841×10^{-1}	1.836×10^{-1}	1.755×10^{-1}	1.713×10^{-1}	1.696×10^{-1}	1.681×10^{-1}
0.85	2.636×10^{-1}	2.277×10^{-1}	2.271×10^{-1}	2.175×10^{-1}	2.126×10^{-1}	2.106×10^{-1}	2.088×10^{-1}
0.90	3.275×10^{-1}	2.857×10^{-1}	2.850×10^{-1}	2.739×10^{-1}	2.680×10^{-1}	2.657×10^{-1}	2.636×10^{-1}
0.95	4.217×10^{-1}	3.780×10^{-1}	3.722×10^{-1}	3.590×10^{-1}	3.521×10^{-1}	3.493×10^{-1}	3.468×10^{-1}
0.99	5.848×10^{-1}	5.259×10^{-1}	5.249×10^{-1}	5.089×10^{-1}	5.005×10^{-1}	4.972×10^{-1}	4.941×10^{-1}

TABLE 5.3 CONTINUED)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{NO_3}}$ = 2.772	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{NO_2}}$ = 2.757	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{Cl}}$ = 2.595	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{I}}$ = 2.578	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{CN}}$ = 2.538	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{Br}}$ = 2.535
0.01	1.538×10^{-5}	1.534×10^{-5}	1.490×10^{-5}	1.486×10^{-5}	1.475×10^{-5}	1.474×10^{-5}
0.05	3.850×10^{-4}	3.840×10^{-4}	3.730×10^{-4}	3.718×10^{-4}	3.691×10^{-4}	3.689×10^{-4}
0.10	1.547×10^{-3}	1.543×10^{-3}	1.499×10^{-3}	1.494×10^{-3}	1.483×10^{-3}	1.482×10^{-3}
0.15	3.507×10^{-3}	3.498×10^{-3}	3.398×10^{-3}	3.387×10^{-3}	3.362×10^{-3}	3.360×10^{-3}
0.20	6.301×10^{-3}	6.285×10^{-3}	6.105×10^{-3}	6.086×10^{-3}	6.041×10^{-3}	6.038×10^{-3}
0.25	9.984×10^{-3}	9.958×10^{-3}	9.673×10^{-3}	9.643×10^{-3}	9.572×10^{-3}	9.566×10^{-3}
0.30	1.463×10^{-2}	1.459×10^{-2}	1.417×10^{-2}	1.413×10^{-2}	1.402×10^{-2}	1.402×10^{-2}
0.35	2.033×10^{-2}	2.028×10^{-2}	1.970×10^{-2}	1.964×10^{-2}	1.949×10^{-2}	1.948×10^{-2}
0.40	2.723×10^{-2}	2.716×10^{-2}	2.638×10^{-2}	2.630×10^{-2}	2.610×10^{-2}	2.609×10^{-2}
0.45	3.548×10^{-2}	3.538×10^{-2}	3.437×10^{-2}	3.427×10^{-2}	3.401×10^{-2}	3.400×10^{-2}
0.50	4.530×10^{-2}	4.519×10^{-2}	4.390×10^{-2}	4.376×10^{-2}	4.344×10^{-2}	4.342×10^{-2}
0.55	5.700×10^{-2}	5.685×10^{-2}	5.523×10^{-2}	5.506×10^{-2}	5.466×10^{-2}	5.463×10^{-2}
0.60	7.094×10^{-2}	7.076×10^{-2}	6.876×10^{-2}	6.855×10^{-2}	6.805×10^{-2}	6.801×10^{-2}
0.65	8.767×10^{-2}	8.744×10^{-2}	8.499×10^{-2}	8.473×10^{-2}	8.412×10^{-2}	8.407×10^{-2}
0.70	1.079×10^{-1}	1.076×10^{-1}	1.047×10^{-1}	1.043×10^{-1}	1.036×10^{-1}	1.035×10^{-1}
0.75	1.327×10^{-1}	1.324×10^{-1}	1.288×10^{-1}	1.284×10^{-1}	1.275×10^{-1}	1.274×10^{-1}
0.80	1.637×10^{-1}	1.633×10^{-1}	1.590×10^{-1}	1.585×10^{-1}	1.574×10^{-1}	1.574×10^{-1}
0.85	2.035×10^{-1}	2.030×10^{-1}	1.979×10^{-1}	1.973×10^{-1}	1.961×10^{-1}	1.960×10^{-1}
0.90	2.573×10^{-1}	2.568×10^{-1}	2.507×10^{-1}	2.500×10^{-1}	2.485×10^{-1}	2.484×10^{-1}
0.95	3.394×10^{-1}	3.388×10^{-1}	3.316×10^{-1}	3.308×10^{-1}	3.290×10^{-1}	3.289×10^{-1}
0.99	4.851×10^{-1}	4.843×10^{-1}	4.755×10^{-1}	4.746×10^{-1}	4.724×10^{-1}	4.722×10^{-1}

TABLE 5.4

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled A(I)-OH(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ						
	$\alpha = \frac{\bar{D}_{IO_3}}{\bar{D}_{OH}}$ =0.204	$\alpha = \frac{\bar{D}_{F}}{\bar{D}_{OH}}$ =0.279	$\alpha = \frac{\bar{D}_{BrO_3}}{\bar{D}_{OH}}$ =0.281	$\alpha = \frac{\bar{D}_{MnO_4}}{\bar{D}_{OH}}$ =0.309	$\alpha = \frac{\bar{D}_{ClO_3}/OCN/CNO}{\bar{D}_{OH}}$ =0.326	$\alpha = \frac{\bar{D}_{SCN}}{\bar{D}_{OH}}$ =0.334	$\alpha = \frac{\bar{D}_{ClO_4}}{\bar{D}_{OH}}$ =0.339
0.01	7.048×10^{-6}	7.397×10^{-6}	7.406×10^{-6}	7.530×10^{-6}	7.605×10^{-6}	7.639×10^{-6}	7.661×10^{-6}
0.05	1.764×10^{-4}	1.852×10^{-4}	1.854×10^{-4}	1.885×10^{-4}	1.904×10^{-4}	1.912×10^{-4}	1.918×10^{-4}
0.10	7.090×10^{-4}	7.441×10^{-4}	7.450×10^{-4}	7.575×10^{-4}	7.650×10^{-4}	7.685×10^{-4}	7.701×10^{-4}
0.15	1.608×10^{-3}	1.687×10^{-3}	1.689×10^{-3}	1.718×10^{-3}	1.735×10^{-3}	1.742×10^{-3}	1.747×10^{-3}
0.20	2.890×10^{-3}	3.033×10^{-3}	3.037×10^{-3}	3.087×10^{-3}	3.118×10^{-3}	3.132×10^{-3}	3.141×10^{-3}
0.25	4.582×10^{-3}	4.808×10^{-3}	4.814×10^{-3}	4.894×10^{-3}	4.942×10^{-3}	4.964×10^{-3}	4.978×10^{-3}
0.30	6.719×10^{-3}	7.049×10^{-3}	7.059×10^{-3}	7.175×10^{-3}	7.246×10^{-3}	7.278×10^{-3}	7.299×10^{-3}
0.35	9.350×10^{-3}	9.808×10^{-3}	9.819×10^{-3}	9.883×10^{-3}	1.008×10^{-2}	1.013×10^{-2}	1.015×10^{-2}
0.40	1.254×10^{-2}	1.315×10^{-2}	1.317×10^{-2}	1.338×10^{-2}	1.351×10^{-2}	1.357×10^{-2}	1.361×10^{-2}
0.45	1.637×10^{-2}	1.717×10^{-2}	1.719×10^{-2}	1.747×10^{-2}	1.764×10^{-2}	1.772×10^{-2}	1.777×10^{-2}
0.50	2.097×10^{-2}	2.198×10^{-2}	2.200×10^{-2}	2.236×10^{-2}	2.258×10^{-2}	2.268×10^{-2}	2.274×10^{-2}
0.55	2.648×10^{-2}	2.774×10^{-2}	2.778×10^{-2}	2.823×10^{-2}	2.850×10^{-2}	2.862×10^{-2}	2.870×10^{-2}
0.60	3.314×10^{-2}	3.470×10^{-2}	3.474×10^{-2}	3.530×10^{-2}	3.563×10^{-2}	3.578×10^{-2}	3.588×10^{-2}
0.65	4.127×10^{-2}	4.317×10^{-2}	4.322×10^{-2}	4.391×10^{-2}	4.431×10^{-2}	4.450×10^{-2}	4.462×10^{-2}
0.70	5.135×10^{-2}	5.367×10^{-2}	5.373×10^{-2}	5.455×10^{-2}	5.505×10^{-2}	5.528×10^{-2}	5.542×10^{-2}
0.75	6.416×10^{-2}	6.696×10^{-2}	6.703×10^{-2}	6.803×10^{-2}	6.863×10^{-2}	6.891×10^{-2}	6.908×10^{-2}
0.80	8.103×10^{-2}	8.438×10^{-2}	8.446×10^{-2}	8.566×10^{-2}	8.638×10^{-2}	8.671×10^{-2}	8.692×10^{-2}
0.85	1.045×10^{-1}	1.084×10^{-1}	1.085×10^{-1}	1.099×10^{-1}	1.108×10^{-1}	1.112×10^{-1}	1.114×10^{-1}
0.90	1.400×10^{-1}	1.444×10^{-1}	1.445×10^{-1}	1.461×10^{-1}	1.471×10^{-1}	1.475×10^{-1}	1.478×10^{-1}
0.95	2.035×10^{-1}	2.074×10^{-1}	2.076×10^{-1}	2.091×10^{-1}	2.101×10^{-1}	2.105×10^{-1}	2.108×10^{-1}
0.99	3.322×10^{-1}	3.332×10^{-1}	3.333×10^{-1}	3.341×10^{-1}	3.347×10^{-1}	3.350×10^{-1}	3.352×10^{-1}

(TABLE 5.4 CONTINUED)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{NO_3}}{\bar{D}_{OH}} = 0.361$	$\alpha = \frac{\bar{D}_{NO_2}}{\bar{D}_{OH}} = 0.363$	$\alpha = \frac{\bar{D}_{Cl}}{\bar{D}_{OH}} = 0.385$	$\alpha = \frac{\bar{D}_{I}}{\bar{D}_{OH}} = 0.387$	$\alpha = \frac{\bar{D}_{CN}}{\bar{D}_{OH}} = 0.394$	$\alpha = \frac{\bar{D}_{Br}}{\bar{D}_{OH}} = 0.395$
0.01	7.755×10^{-6}	7.764×10^{-6}	7.856×10^{-6}	7.865×10^{-6}	7.898×10^{-6}	7.898×10^{-6}
0.05	1.941×10^{-4}	1.943×10^{-4}	1.967×10^{-4}	1.969×10^{-4}	1.976×10^{-4}	1.977×10^{-4}
0.10	7.801×10^{-4}	7.809×10^{-4}	7.903×10^{-4}	7.911×10^{-4}	7.940×10^{-4}	7.945×10^{-4}
0.15	1.769×10^{-3}	1.771×10^{-3}	1.792×10^{-3}	1.794×10^{-3}	1.800×10^{-3}	1.801×10^{-3}
0.20	3.179×10^{-3}	3.183×10^{-3}	3.221×10^{-3}	3.224×10^{-3}	3.236×10^{-3}	3.238×10^{-3}
0.25	5.039×10^{-3}	5.045×10^{-3}	5.105×10^{-3}	5.110×10^{-3}	5.129×10^{-3}	5.132×10^{-3}
0.30	7.388×10^{-3}	7.396×10^{-3}	7.484×10^{-3}	7.492×10^{-3}	7.519×10^{-3}	7.523×10^{-3}
0.35	1.028×10^{-2}	1.029×10^{-2}	1.041×10^{-2}	1.042×10^{-2}	1.046×10^{-2}	1.046×10^{-2}
0.40	1.378×10^{-2}	1.379×10^{-2}	1.395×10^{-2}	1.397×10^{-2}	1.402×10^{-2}	1.403×10^{-2}
0.45	1.798×10^{-2}	1.800×10^{-2}	1.821×10^{-2}	1.823×10^{-2}	1.830×10^{-2}	1.831×10^{-2}
0.50	2.301×10^{-2}	2.304×10^{-2}	2.330×10^{-2}	2.333×10^{-2}	2.341×10^{-2}	2.343×10^{-2}
0.55	2.904×10^{-2}	2.907×10^{-2}	2.941×10^{-2}	2.944×10^{-2}	2.954×10^{-2}	2.956×10^{-2}
0.60	3.630×10^{-2}	3.634×10^{-2}	3.676×10^{-2}	3.679×10^{-2}	3.692×10^{-2}	3.694×10^{-2}
0.65	4.514×10^{-2}	4.518×10^{-2}	4.569×10^{-2}	4.574×10^{-2}	4.590×10^{-2}	4.592×10^{-2}
0.70	5.605×10^{-2}	5.611×10^{-2}	5.673×10^{-2}	5.678×10^{-2}	5.698×10^{-2}	5.701×10^{-2}
0.75	6.984×10^{-2}	6.991×10^{-2}	7.066×10^{-2}	7.072×10^{-2}	7.096×10^{-2}	7.099×10^{-2}
0.80	8.783×10^{-2}	8.792×10^{-2}	8.882×10^{-2}	8.890×10^{-2}	8.918×10^{-2}	8.922×10^{-2}
0.85	1.125×10^{-1}	1.126×10^{-1}	1.137×10^{-1}	1.138×10^{-1}	1.141×10^{-1}	1.141×10^{-1}
0.90	1.490×10^{-1}	1.492×10^{-1}	1.504×10^{-1}	1.505×10^{-1}	1.509×10^{-1}	1.509×10^{-1}
0.95	2.121×10^{-1}	2.122×10^{-1}	2.135×10^{-1}	2.136×10^{-1}	2.140×10^{-1}	2.140×10^{-1}
0.99	3.362×10^{-1}	3.363×10^{-1}	3.373×10^{-1}	3.374×10^{-1}	3.377×10^{-1}	3.378×10^{-1}

TABLE 5.5

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled OH(I)-A(II) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(T)$	Dimensionless time, T					
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{HPO_4}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_4}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{CO_3}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{WO_4}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{C_2O_4}}$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SeO_4}}$
	= 6.000	= 2.977	= 2.920	= 2.869	= 2.770	= 2.615
0.01	1.856×10^{-5}	1.405×10^{-5}	1.395×10^{-5}	1.386×10^{-5}	1.369×10^{-5}	1.342×10^{-5}
0.05	4.646×10^{-4}	3.516×10^{-4}	3.492×10^{-4}	3.417×10^{-4}	3.427×10^{-4}	3.359×10^{-4}
0.10	1.867×10^{-3}	1.413×10^{-3}	1.403×10^{-3}	1.394×10^{-3}	1.377×10^{-3}	1.350×10^{-3}
0.15	4.232×10^{-3}	3.202×10^{-3}	3.180×10^{-3}	3.160×10^{-3}	3.121×10^{-3}	3.059×10^{-3}
0.20	7.604×10^{-3}	5.752×10^{-3}	5.712×10^{-3}	5.677×10^{-3}	5.606×10^{-3}	5.495×10^{-3}
0.25	1.205×10^{-2}	9.111×10^{-3}	9.048×10^{-3}	8.991×10^{-3}	8.880×10^{-3}	8.704×10^{-3}
0.30	1.765×10^{-2}	1.334×10^{-2}	1.325×10^{-2}	1.317×10^{-2}	1.301×10^{-2}	1.275×10^{-2}
0.35	2.453×10^{-2}	1.854×10^{-2}	1.841×10^{-2}	1.830×10^{-2}	1.807×10^{-2}	1.771×10^{-2}
0.40	3.283×10^{-2}	2.481×10^{-2}	2.464×10^{-2}	2.449×10^{-2}	2.418×10^{-2}	2.370×10^{-2}
0.45	4.276×10^{-2}	3.231×10^{-2}	3.209×10^{-2}	3.189×10^{-2}	3.149×10^{-2}	3.087×10^{-2}
0.50	5.458×10^{-2}	4.124×10^{-2}	4.095×10^{-2}	4.069×10^{-2}	4.019×10^{-2}	3.940×10^{-2}
0.55	6.862×10^{-2}	5.184×10^{-2}	5.149×10^{-2}	5.116×10^{-2}	5.054×10^{-2}	4.954×10^{-2}
0.60	8.531×10^{-2}	6.448×10^{-2}	6.404×10^{-2}	6.364×10^{-2}	6.286×10^{-2}	6.163×10^{-2}
0.65	1.053×10^{-1}	7.964×10^{-2}	7.909×10^{-2}	7.860×10^{-2}	7.765×10^{-2}	7.613×10^{-2}
0.70	1.293×10^{-1}	9.797×10^{-2}	9.731×10^{-2}	9.671×10^{-2}	9.555×10^{-2}	9.370×10^{-2}
0.75	1.585×10^{-1}	1.205×10^{-1}	1.197×10^{-1}	1.189×10^{-1}	1.175×10^{-1}	1.153×10^{-1}
0.80	1.947×10^{-1}	1.487×10^{-1}	1.477×10^{-1}	1.468×10^{-1}	1.491×10^{-1}	1.424×10^{-1}
0.85	2.406×10^{-1}	1.851×10^{-1}	1.839×10^{-1}	1.829×10^{-1}	1.808×10^{-1}	1.776×10^{-1}
0.90	3.019×10^{-1}	2.348×10^{-1}	2.334×10^{-1}	2.322×10^{-1}	2.297×10^{-1}	2.258×10^{-1}
0.95	3.941×10^{-1}	3.119×10^{-1}	3.102×10^{-1}	3.086×10^{-1}	3.056×10^{-1}	3.009×10^{-1}
0.99	5.562×10^{-1}	4.512×10^{-1}	4.490×10^{-1}	4.471×10^{-1}	4.433×10^{-1}	4.373×10^{-1}

(TABLE 5.5. CONTINUED)

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{CrO_4}} = 2.500$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SO_3}} = 2.478$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{SO_4}} = 2.475$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_3}} = 2.329$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_8}} = 2.302$	$\alpha = \frac{\bar{D}_{OH}}{\bar{D}_{S_2O_6}} = 2.129$
0.01	1.321×10^{-5}	1.317×10^{-5}	1.317×10^{-5}	1.290×10^{-5}	1.285×10^{-5}	1.253×10^{-5}
0.05	3.308×10^{-4}	3.298×10^{-4}	3.296×10^{-4}	3.230×10^{-4}	3.217×10^{-4}	3.136×10^{-4}
0.10	1.329×10^{-3}	1.324×10^{-3}	1.324×10^{-3}	1.298×10^{-3}	1.293×10^{-3}	1.260×10^{-3}
0.15	3.012×10^{-3}	3.002×10^{-3}	3.002×10^{-3}	2.941×10^{-3}	2.930×10^{-3}	2.856×10^{-3}
0.20	$5,411\times10^{-3}$	5.395×10^{-3}	5.393×10^{-3}	5.264×10^{-3}	5.263×10^{-3}	5.131×10^{-3}
0.25	8.571×10^{-3}	8.545×10^{-3}	8.541×10^{-3}	8.369×10^{-3}	8.337×10^{-3}	8.127×10^{-3}
0.30	1.255×10^{-2}	1.252×10^{-2}	1.251×10^{-2}	1.226×10^{-2}	1.221×10^{-2}	1.190×10^{-2}
0.35	1.744×10^{-2}	1.739×10^{-2}	1.738×10^{-2}	1.703×10^{-2}	1.697×10^{-2}	1.654×10^{-2}
0.40	2.334×10^{-2}	2.327×10^{-2}	2.326×10^{-2}	2.279×10^{-2}	2.271×10^{-2}	2.214×10^{-2}
0.45	3.040×10^{-2}	3.031×10^{-2}	3.030×10^{-2}	2.969×10^{-2}	2.957×10^{-2}	2.883×10^{-2}
0.50	3.880×10^{-2}	3.868×10^{-2}	3.867×10^{-2}	3.789×10^{-2}	3.775×10^{-2}	3.680×10^{-2}
0.55	4.879×10^{-2}	4.864×10^{-2}	4.862×10^{-2}	4.765×10^{-2}	4.747×10^{-2}	4.629×10^{-2}
0.60	6.070×10^{-2}	6.052×10^{-2}	6.049×10^{-2}	5.929×10^{-2}	5.906×10^{-2}	5.760×10^{-2}
0.65	7.499×10^{-2}	7.477×10^{-2}	7.474×10^{-2}	7.326×10^{-2}	7.298×10^{-2}	7.119×10^{-2}
0.70	9.230×10^{-2}	9.204×10^{-2}	9.200×10^{-2}	9.020×10^{-2}	8.986×10^{-2}	8.768×10^{-2}
0.75	1.136×10^{-1}	1.133×10^{-1}	1.32×10^{-1}	1.111×10^{-1}	1.106×10^{-1}	1.080×10^{-1}
0.80	1.404×10^{-1}	1.400×10^{-1}	1.399×10^{-1}	1.373×10^{-1}	1.368×10^{-1}	1.338×10^{-1}
0.85	1.791×10^{-1}	1.746×10^{-1}	1.746×10^{-1}	1.714×10^{-1}	1.708×10^{-1}	1.670×10^{-1}
0.90	2.228×10^{-1}	2.223×10^{-1}	2.222×10^{-1}	2.184×10^{-1}	2.177×10^{-1}	2.132×10^{-1}
0.95	2.973×10^{-1}	2.966×10^{-1}	2.965×10^{-1}	2.920×10^{-1}	2.911×10^{-1}	2.857×10^{-1}
0.99	4.328×10^{-1}	4.320×10^{-1}	4.319×10^{-1}	4.262×10^{-1}	4.251×10^{-1}	4.184×10^{-1}

TABLE 5.6

Dimensionless time as a function of fractional attainment of equilibrium for some particle diffusion controlled A(II)-OH(I) exchanges involving different mobility ratios

Fractional attainment of equilibrium $U(\tau)$	Dimensionless time, τ					
	$\alpha = \frac{\bar{D}_{HPO_4}}{\bar{D}_{OH}} = 0.170$	$\alpha = \frac{\bar{D}_{S_2O_4}}{\bar{D}_{OH}} = 0.336$	$\alpha = \frac{\bar{D}_{CO_3}}{\bar{D}_{OH}} = 0.340$	$\alpha = \frac{\bar{D}_{WO_4}}{\bar{D}_{OH}} = 0.348$	$\alpha = \frac{\bar{D}_{C_2O_4}}{\bar{D}_{OH}} = 0.360$	$\alpha = \frac{\bar{D}_{SeO_4}}{\bar{D}_{OH}} = 0.382$
0.01	4.982×10^{-6}	6.126×10^{-6}	6.152×10^{-6}	6.205×10^{-6}	6.283×10^{-6}	6.426×10^{-6}
0.05	1.248×10^{-4}	1.534×10^{-4}	1.541×10^{-4}	1.554×10^{-4}	1.573×10^{-4}	1.609×10^{-4}
0.10	5.027×10^{-4}	6.170×10^{-4}	6.197×10^{-4}	6.202×10^{-4}	6.328×10^{-4}	6.472×10^{-4}
0.15	1.144×10^{-3}	1.402×10^{-3}	1.408×10^{-3}	1.419×10^{-3}	1.437×10^{-3}	1.469×10^{-3}
0.20	2.068×10^{-3}	2.526×10^{-3}	2.536×10^{-3}	2.557×10^{-3}	2.589×10^{-3}	2.646×10^{-3}
0.25	3.302×10^{-3}	4.016×10^{-3}	4.033×10^{-3}	4.066×10^{-3}	4.116×10^{-3}	4.206×10^{-3}
0.30	4.886×10^{-3}	5.912×10^{-3}	5.936×10^{-3}	5.984×10^{-3}	6.056×10^{-3}	6.186×10^{-3}
0.35	6.875×10^{-3}	8.266×10^{-3}	8.298×10^{-3}	8.363×10^{-3}	8.461×10^{-3}	8.639×10^{-3}
0.40	9.341×10^{-3}	1.115×10^{-2}	1.119×10^{-2}	1.127×10^{-2}	1.140×10^{-2}	1.163×10^{-2}
0.45	1.238×10^{-2}	1.464×10^{-2}	1.470×10^{-2}	1.481×10^{-2}	1.497×10^{-2}	1.526×10^{-2}
0.50	1.614×10^{-2}	1.888×10^{-2}	1.895×10^{-2}	1.908×10^{-2}	1.928×10^{-2}	1.965×10^{-2}
0.55	2.077×10^{-2}	2.403×10^{-2}	2.411×10^{-2}	2.417×10^{-2}	2.451×10^{-2}	2.496×10^{-2}
0.60	2.648×10^{-2}	3.030×10^{-2}	3.040×10^{-2}	3.059×10^{-2}	3.088×10^{-2}	3.141×10^{-2}
0.65	3.347×10^{-2}	3.799×10^{-2}	3.810×10^{-2}	3.832×10^{-2}	3.866×10^{-2}	3.930×10^{-2}
0.70	4.332×10^{-2}	5.000×10^{-2}	5.015×10^{-2}	5.045×10^{-2}	5.090×10^{-2}	5.172×10^{-2}
0.75	5.437×10^{-2}	6.245×10^{-2}	6.264×10^{-2}	6.301×10^{-2}	6.355×10^{-2}	6.555×10^{-2}
0.80	6.915×10^{-2}	7.887×10^{-2}	7.909×10^{-2}	7.954×10^{-2}	8.020×10^{-2}	8.141×10^{-2}
0.85	9.021×10^{-2}	1.017×10^{-1}	1.020×10^{-1}	1.025×10^{-1}	1.033×10^{-1}	1.048×10^{-1}
0.90	1.236×10^{-1}	1.366×10^{-1}	1.369×10^{-1}	1.376×10^{-1}	1.385×10^{-1}	1.402×10^{-1}
0.95	1.890×10^{-1}	2.001×10^{-1}	2.005×10^{-1}	2.011×10^{-1}	2.020×10^{-1}	2.038×10^{-1}
0.99	3.327×10^{-1}	3.337×10^{-1}	3.338×10^{-1}	3.342×10^{-1}	3.348×10^{-1}	3.359×10^{-1}

(TABLE 5.6 CONTINUED)

Fractional attainment of equilibrium $U(\Upsilon)$	Dimensionless time, Υ				
	$\alpha = \frac{\bar{D}_{CrO_4}}{\bar{D}_{OH}}$ = 0.400	$\alpha = \frac{\bar{D}_{SO_3/SO_4}}{\bar{D}_{OH}}$ = 0.404	$\alpha = \frac{\bar{D}_{S_2O_3}}{\bar{D}_{OH}}$ = 0.429	$\alpha = \frac{\bar{D}_{S_2O_8}}{\bar{D}_{OH}}$ = 0.434	$\alpha = \frac{\bar{D}_{S_2O_6}}{\bar{D}_{OH}}$ = 0.469
0.01	6.543×10^{-6}	6.568×10^{-6}	6.729×10^{-6}	6.760×10^{-6}	6.982×10^{-6}
0.05	1.638×10^{-4}	1.645×10^{-4}	1.685×10^{-4}	1.693×10^{-4}	1.748×10^{-4}
0.10	6.588×10^{-4}	6.614×10^{-4}	6.774×10^{-4}	6.806×10^{-4}	7.028×10^{-4}
0.15	1.496×10^{-3}	1.502×10^{-3}	1.538×10^{-3}	1.545×10^{-3}	1.595×10^{-3}
0.20	2.693×10^{-3}	2.703×10^{-3}	2.768×10^{-3}	2.781×10^{-3}	2.871×10^{-3}
0.25	4.279×10^{-3}	4.296×10^{-3}	4.397×10^{-3}	4.417×10^{-3}	4.558×10^{-3}
0.30	6.292×10^{-3}	6.316×10^{-3}	6.462×10^{-3}	6.492×10^{-3}	6.695×10^{-3}
0.35	8.784×10^{-3}	8.817×10^{-3}	9.017×10^{-3}	9.057×10^{-3}	9.337×10^{-3}
0.40	1.182×10^{-2}	1.187×10^{-2}	1.213×10^{-2}	1.218×10^{-2}	1.255×10^{-2}
0.45	1.551×10^{-2}	1.556×10^{-2}	1.590×10^{-2}	1.596×10^{-2}	1.643×10^{-2}
0.50	1.995×10^{-2}	2.002×10^{-2}	2.044×10^{-2}	2.052×10^{-2}	2.111×10^{-2}
0.55	2.532×10^{-2}	2.541×10^{-2}	2.592×10^{-2}	2.602×10^{-2}	2.674×10^{-2}
0.60	3.185×10^{-2}	3.194×10^{-2}	3.256×10^{-2}	3.268×10^{-2}	3.355×10^{-2}
0.65	3.982×10^{-2}	3.993×10^{-2}	4.302×10^{-2}	4.316×10^{-2}	4.419×10^{-2}
0.70	5.238×10^{-2}	5.253×10^{-2}	5.344×10^{-2}	5.362×10^{-2}	5.488×10^{-2}
0.75	6.536×10^{-2}	6.554×10^{-2}	6.664×10^{-2}	6.686×10^{-2}	6.839×10^{-2}
0.80	8.238×10^{-2}	8.260×10^{-2}	8.394×10^{-2}	8.421×10^{-2}	8.606×10^{-2}
0.85	1.060×10^{-1}	1.062×10^{-1}	1.078×10^{-1}	1.082×10^{-1}	1.104×10^{-1}
0.90	1.416×10^{-1}	1.419×10^{-1}	1.438×10^{-1}	1.442×10^{-1}	1.468×10^{-1}
0.95	2.053×10^{-1}	2.056×10^{-1}	2.076×10^{-1}	2.080×10^{-1}	2.109×10^{-1}
0.99	3.369×10^{-1}	3.372×10^{-1}	3.387×10^{-1}	3.390×10^{-1}	3.413×10^{-1}

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AUTHOR(s) :

K.G. Varshney; A. Ahmad;
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